# TEMPERATURE DEPENDENCE OF EXCESS THERMODYNAMIC PROPERTIES OF ETHANOL + n-HEPTANE AND 2-PROPANOL + n-HEPTANE SOLUTIONS

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7/25/68

# DEDICATION

To my wife, Barbsie, and daughter, Carey

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I extend my sincere appreciation to Dr. W. T. Ziegler, who has been responsible for developing my proficiency in experimental technique and for my much improved understanding of thermodynamics. The completion of this thesis is only possible because of the advice, guidance, and time that he has given to me.

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| | |
|---|---|
| C | molar heat capacity or concentration |
| F | per cent melted |
| G | molar Gibbs free energy |
| H | molar enthalpy |
| HA | molar enthalpy of hydrogen bonding, Wiehe-Bagley equation |
| $H^{o}$ | molar enthalpy of hydrogen bond, volume fraction model |
| $H_2$ | molar enthalpy of hydrogen bond for dimer, mole fraction model |
| $H_3$ | molar enthalpy of hydrogen bond for i-mer, $i > 1$, mole fraction model |
| h | molar enthalpy of hydrogen bond for i-mer, mole fraction model, $[i(R\text{-}OH) \rightleftarrows (R\text{-}OH)_i]$ |
| J | average chain length of monomer alcohols units |
| K | equilibrium constant for $[R\text{-}OH + (R\text{-}OH)_i \rightleftarrows (R\text{-}OH)_{i+1}]$ |
| $K_2$ | equilibrium constant for dimer reaction, mole fraction model |
| $K_3$ | equilibrium constant for i-mer reaction, $i \neq 1$, mole fraction model |
| KA | equilibrium constant, Wiehe-Bagley equation |
| k | equilibrium constant for $[i(R\text{-}OH) \rightleftarrows (R\text{-}OH)_i]$, mole fraction model |
| Ln | natural logarith |
| n | moles (for mole fraction model, $n = n_a + n_n$ = stoichiometric number of moles) |
| R | gas law constant |
| S | molar entropy |
| SA | molar entropy of hydrogen bonding divided by R, Wiehe-Bagley equation |

## LIST OF SYMBOLS (Continued)

| | |
|---|---|
| SQRT | denotes the mathematical square root operation |
| $T$ | Kelvins |
| t | degree Celsius |
| v | molar volume |
| X | any extensive thermodynamic molar quantity |
| x | mole fraction |

GREEK ALPHABET

| | |
|---|---|
| $\beta$ | physical interaction parameter |
| $\gamma$ | activity coefficient |
| $\Delta$ | difference or change |
| $\mu$ | chemical potential |
| $\Phi$ | volume fraction |
| $\rho$ | adjustable parameter, Wiehe-Bagley equation |
| $\Sigma$ | summation |
| $\tau$ | symmetry number |
| $\theta$ | coordination number for the lattice |

SUBSCRIPTS

| | |
|---|---|
| a | of stoichiometric alcohol |
| av | average |
| c | of chemical interaction effect due to the breaking of hydrogen bonds |
| e | at equilibrium |
| f | of fusion |

## LIST OF SYMBOLS (Continued)

| | |
|---|---|
| h | of stoichiometric hydrocarbon |
| i | of i-mer (i = 1,2,...,i) |
| j | of component j |
| mp | of melting point |
| P | at constant pressure |
| p | of physical interaction effect |
| sat | under conditions of saturation |
| T | at constant temperature |

SUPERSCRIPTS

| | |
|---|---|
| E | excess property (Note - derived excess property implies derived from the experimental excess heat capacity) |
| f | final mixed state |
| i | initial unmixed state, pure component |
| id | ideal solution |
| M | property of mixing |
| o | property of pure species |
| oo | property of pure species in oriented state |
| S | property of solution or mixture |

## SUMMARY

The objectives of this work were: (1) to determine experimentally the composition and temperature dependence of the excess heat capacity, $C_p^E$, excess enthalpy, $H^E$, excess entropy, $S^E$, and excess Gibbs free energy, $G^E$, for two alcohol-hydrocarbon systems (ethanol + n-heptane and 2-propanol + n-heptane) over a wide temperature range, and (2) to use these excess thermodynamic property data to test the current theories of associated solutions.

The excess heat capacity was determined from experimental measurements of the heat capacities of the pure components and of binary mixtures in a precision adiabatic-shield high-vacuum calorimeter. The purity and melting point of each pure component were also measured in the calorimeter. From the excess heat capacity data the other excess properties were calculated by means of appropriate thermodynamic relations.

The heat capacities of ethanol, 2-propanol, and n-heptane were measured from 159 to 306 K, 185 to 304 K, and 182 to 302 K, respectively. The melting points of pure ethanol, 2-propanol, and n-heptane were found to be 158.991 K, 185.232 K, and 182.562 K. The heat capacity of ethanol + n-heptane was measured from 215 to 305 K at mole fractions of ethanol of 0.1023, 0.2805, 0.4388, 0.6140, and 0.8107. The heat capacity of 2-propanol + n-heptane was measured from 187 to 305 K at mole fractions of 2-propanol of 0.0809, 0.2492, 0.4219, 0.5993, and 0.7984. The excess heat capacity of each mixture was calculated from

the heat capacity of the pure components and of the mixtures. The heat capacity measurements were estimated to be accurate to 0.2 per cent. The excess heat capacity was determined to be accurate to 0.15 to 0.07 Joules/gm. mole-K from pure n-heptane to pure alcohol. The heat capacities of the pure components have been measured by other investigators[1,10,21,34,55]. The present work agreed with those measurements within experimental error.

The excess enthalpy and excess Gibbs free energy have been measured by other investigators at 303.15 K for ethanol + n-heptane[60] and 2-propanol + n-heptane[59]. The excess heat capacity data were used in conjunction with these data at 303.15 K to derive the other excess properties. The properties $H^E$, $G^E$, $S^E$, and Gibbs free energy of mixing were derived in the present work at five degree intervals from 183 to 318 K for ethanol + n-heptane and from 163 to 318 K for 2-propanol + n-heptane.

The excess thermodynamic properties of ethanol + n-heptane and their observed temperature dependence can be summarized as follows. The excess heat capacity is positive except at low temperatures in the alcohol rich composition range. The excess heat capacity is the slope of the temperature variation of the excess enthalpy. The excess enthalpy has a maximum of 675 Joules/gm. mole at 303.15 K decreasing to 289 Joules/gm. mole at 213.15 K. The maximum shifts from an alcohol mole fraction of 0.38 at 303.15 K to 0.65 at 213.15 K. The excess entropy is negative except at high temperatures in the dilute alcohol region. The minimum of -2.6 Joules/gm. mole-K at 303.15 K and 0.52 mole fraction alcohol decreases to -4.1 Joules/gm. mole-K at 213.15 K

and 0.44 mole fraction alcohol. The excess Gibbs free energy is symmetrical with a maximum of 1450 Joules/gm. mole at 303.15 K decreasing to 1120 Joules/gm. mole at 213.15 K.

The excess thermodynamic properties of 2-propanol + n-heptane and their observed temperature dependence can be summarized as follows. The excess heat capacity is positive except at low temperatures in the alcohol rich composition range. The excess enthalpy has a maximum of 910 Joules/mole at 303.15 K decreasing to 225 Joules/mole at 213.15 K. The maximum shifts from an alcohol mole fraction of 0.40 at 303.15 K to 0.7 at 183.15 K. The excess entropy is negative except at high temperatures in the dilute alcohol region. The minimum of -1.28 Joules/mole-K at 303.15 K and 0.58 mole fraction alcohol decreases to -3.84 Joules/mole-K at 183.15 K and 0.41 mole fraction alcohol. The excess Gibbs free energy is symmetrical with a maximum of 1260 Joules/mole at 303.15 K decreasing to 895 Joules/mole at 183.15 K.

The excess properties of the two systems and their observed temperature dependence are similar. The excess enthalpy of the 2-propanol system, however, is larger than that of the ethanol system. This larger excess enthalpy of the 2-propanol system at 303.15 K is necessarily an entropy or Gibbs free energy effect. However, the excess Gibbs free energy of the system is actually smaller; therefore the larger excess enthalpy is due to a larger entropy difference than is present in the ethanol system. It was anticipated that measurements at lower temperatures would elucidate this effect. This was not the case, since the entropy difference decreased rapidly with temperature.

The Gibbs free energy of mixing versus composition indicates that ethanol + n-heptane definitely separates into two phases even if the uncertainty of the derived $\Delta G^M$ data is considered. The indication for 2-propanol + n-heptane was uncertain within experimental error. Qualitative cloud point experiments verified that 2-propanol + n-heptane freezes before it separates and that ethanol + n-heptane has an upper critical solution temperature at 207.6 $\pm$ 0.5 K and 0.43 mole fraction ethanol. The phase separation is very sensitive to the presence of water.

The excess Gibbs free energy data of ethanol + n-heptane and 2-propanol + n-heptane were correlated with three empirical equations and one semi-empirical equation. The methods considered were the Redlich-Kister equation,[35] a modified form of the Redlich-Kister equation,[35] the Wilson equation,[64] and the Wiehe-Bagley equation.[62]

The Redlich-Kister equation fits the $G^E$ data to an average deviation of better than 0.5 per cent with four parameters. In contrast the "modified" Redlich-Kister equation fits the $G^E$ data with an average deviation of 0.4 per cent or less, with as many or fewer parameters. Since the constants of each equation are a function of temperature only; the data for each constant were fitted with a power series in temperature. The result was a representation of the $G^E$-T-x surface. These functions are recommended for interpolation purposes.

The two-parameter Wilson equation fits the $G^E$ data as well as either of the Redlich-Kister equations for the ethanol + n-heptane system but not as well for the 2-propanol + n-heptane system. In fact the average deviation for the 2-propanol + n-heptane system was as

large as 2 per cent at 303.15 K.

The Wiehe-Bagley relation is rigorously derivable from a theoretical model in which only the major interaction of the breaking of the hydrogen bonds is considered. The Wiehe-Bagley equation fits the $G^E$ data as well as the empirical ones at 303.15 K. At lower temperatures the Wiehe-Bagley equation represents the data for the two alcohol-hydrocarbon systems less satisfactorily. This is attributed to the fact that the effect of the breaking of the hydrogen bonds becomes less important than physical interactions (not considered in the analysis of Wiehe and Bagley) at the lower temperatures. The determination of the parameters for the Wiehe-Bagley equation required no excess enthalpy data. However the excess enthalpy can be calculated by the proper differentiation of the excess Gibbs free energy. The excess enthalpy data were calculated for both alcohol-hydrocarbon systems and gave a rough qualitative representation of the derived $H^E$ data.

The excess Gibbs free energy and excess enthalpy were also correlated by two current variations of the theory of associated solutions with the inclusion of the concept of continuous association[18,44]. The first is a volume fraction model which considers two interactions: (1) a chemical interaction related to the breaking of the hydrogen bonds is characterized by one equilibrium constant, K, and one enthalpy of formation of a hydrogen bond, $H^o$, and (2) a physical interaction of the van der Waals type is characterized by one temperature dependent parameter, $\beta$. The parameters were determined for the ethanol + n-heptane and ethanol + methylcyclohexane systems at 213.15, 243.15, 273.15, and 303.15 K and for the 2-propanol + n-heptane system

at 183.15, 213.15, 243.15, 273.15, and 303.15 K. Three modifications of the volume fraction model were investigated. These include 1) varying $H^{o}$ but keeping it temperature independent, 2) varying K at 50°C, and 3) making $H^{o}$ linearly temperature dependent

$$H^{o} = H^{o}(323.15) + A\cdot(T - 323.15) \quad .$$

The first two modifications resulted in no improvement in the overall correlation of the excess properties. The third modification did not warrant the addition of a new adjustable parameter. The model has been used by Renon and Prausnitz[44] to correlate excess thermodynamic data at and above room temperature. The second variation is a mole fraction model which considers only the chemical interaction related to the breaking of a hydrogen bond. This model is characterized by an equilibrium constant, $K_2$, and a temperature dependent enthalpy of formation, $H_2$, for the formation of a dimer and by a equilibrium constant, $K_3$, and a temperature dependent enthalpy of formation, $H_3$, for the formation of an i+1-mer from a monomer and an i-mer. The constants were determined for ethanol + n-heptane at 213.15, 243.15, 273.15, and 303.15 K. The model has been used by Haskell et al.[18] to correlate excess thermodynamic data at and above room temperature.

The correlation of the excess thermodynamic data with the volume fraction model can be summarized as follows. The contribution to the excess enthalpy due to the breaking of hydrogen bonds decreases with decreasing temperature and becomes negligible at the lowest temperature. The observed decrease of the effect was attributed to an increase

in the equilibrium constant which suggests that higher order i-mers are favored at lower temperatures. The contribution due to physical interactions increases slightly with decreasing temperature.

The correlation of the excess thermodynamic data with the mole fraction model can be summarized as follows. The contribution to the excess enthalpy due to the breaking of hydrogen bonds also decreases with decreasing temperature. This model predicts a larger contribution to this effect at lower temperatures than does the volume fraction model. The results of the theoretical analysis with the mole fraction model suggested that a modification be made to include a physical interaction term.

The present work combined with the works of Renon and Prausnitz[44], and of Haskell et al.[17] represent a very extensive theoretical analysis of the excess thermodynamic data of the ethanol + n-heptane system from 213.15 to 348.15 K. The volume fraction model gave the better correlation especially at lower temperatures. It was concluded that, for the sake of mathematical simplicity without the loss of a reasonable interpretation of the experimental data, that the volume fraction model be used.

# CHAPTER I

## INTRODUCTION

The theory of solutions of nonelectrolytes has been the subject of discussion and research for many years. In the past few decades a concentrated study has been directed to the study of solutions in which specific strong interactions occur. Specifically, solutions of alcohol-inert solvents have attracted a lot of interest because the strong non-ideality that they exhibit can be attributed to hydrogen bonding.

Excess thermodynamic properties have been a successful approach to the study of these specific interactions. Two different theoretical approaches have proven useful in analyzing these excess property data. One approach has been developed by Barker[3,4] and Tompa[58] based on a quasi-lattice picture of the liquid, where each molecule occupies a certain number of sites of a lattice. The other approach has been the "theory of associated solutions" which is based on a quasi-chemical idea first introduced by Dolezalek[9] and since then has been improved by several authors[18,22,29,38,43,44]. The quasi-chemical theory attributes the major effect of chemical interaction to the alcohol molecule, which forms associated polymeric species by chemical reactions.

The objectives of this work have been: (1) to determine experimentally the composition and temperature dependence of the excess heat capacity, $C_p^E$, excess enthalpy, $H^E$, excess entropy, $S^E$, and excess Gibbs free energy, $G^E$, for two alcohol-hydrocarbon systems (ethanol + n-heptane

and 2-propanol + n-heptane) over a temperature range from room temperature to -90°C and (2) to use these excess property data to test the current theory of associated solutions.

The excess thermodynamic properties $C_p^E$, $H^E$, $S^E$, and $G^E$ are all interrelated thermodynamically as given by Equations (6), (7), and (8) of Chapter IV. Therefore, from an experimental determination of the temperature dependence of one of the properties, the others can be calculated provided the necessary integration constants are available. The $G^E$ data are generally calculated from vapor-liquid equilibrium measurements. At these lower temperatures the vapor pressure is too low to be measured accurately with present day techniques. The $C_p^E$ and $H^E$ data, however, can be determined directly from experimental measurements. The $H^E$ measurement is more suitable for the determination of the compositional dependence at an isotherm and the $C_p^E$ measurement is more suitable for the determination of the temperature dependence at constant composition. For this reason and the availability of the equipment, the excess heat capacity has been determined from measurements of the heat capacity of the pure components and five binary mixtures for each system in a precision adiabatic calorimeter suitable for measurements from 15 to 350 K.

An extensive review of the literature has been made to determine the excess enthalpy and excess heat capacity data that have been measured for binary nonelectrolyte mixtures. As a result of this literature search, two unpublished compilations were made, one for $H^E$ and one for $C_p^E$. The excess enthalpy compilation contains more than 700 binary

systems of published and unpublished data. The data have been classified in one of three classes (Non-Polar + Non-Polar, Non-Polar + Polar, or Polar + Polar) according to the overall dipole moment of the components. A similar compilation has been made of the heat capacity of mixtures but only about 50 mixtures have been measured. A review of the heat capacity measurements of binary solutions has been made by Rowlinson[49]. Recent excess heat capacity measurements include those of Hwa[22], Chang and Westrum[5], and of Klesper[26]. Chang and Westrum studied carbon tetrachloride + tetramethylmethane over a wide temperature range extending into the solid region. However, they failed to measure the heat capacity of the pure components. Klesper studied two alcohol-hydrocarbon solutions but over a very limited temperature range near room temperature. Hwa made a study of ethanol + methylcyclohexane and ethanol + toluene over a wide temperature range. In fact his work initiated the interest in the present set of measurements. A compilation of the excess Gibbs free energy or vapor-liquid equilibrium data has been given elsewhere[6,16].

The literature search served a twofold purpose. It served as a guide in choosing the systems that were studied and it afforded the knowledge of the availability of the excess Gibbs free energy and excess enthalpy at one temperature to be used as integration constants. The integration constants, $H^E$ and $G^E$, are available for the systems to be studied (ethanol + n-heptane[60] and 2-propanol + n-heptane[59]). The excess heat capacity data and the integration constants are used to calculate $H^E$, $S^E$, and $G^E$ as a function of temperature. The present excess thermodynamic study from room temperature to -90°C complements the previous studies of Van Ness and his colleagues[18,59,60] from room

temperature up to 75°C. As a result excess thermodynamic data are available for two alcohol-hydrocarbon systems over a very wide temperature range.

The theory of associated solutions has been chosen for study. Two variations of this theory have been investigated. One model is based on volume fraction statistics and the other on mole fraction statistics. Both models are based on the concept of continuous association. This concept allows the existence of polymeric alcohol species with a chain length from one to infinity. The volume fraction model separates the interactions into chemical and physical types. The parameters of this model include one equilibrium constant independent of the polymeric reaction, an enthalpy of formation of a hydrogen bond independent of temperature, and a temperature dependent physical interaction parameter. The mole fraction model, on the other hand, recognizes only chemical interactions. The parameters of this model include an equilibrium constant for the dimerization reaction only, an equilibrium constant for higher order reactions independent of the polymer formed, and an enthalpy of formation of a hydrogen bond with a linear dependence of temperature.

# CHAPTER II

## EXPERIMENTAL APPARATUS AND PROCEDURE

### Description of Apparatus

The apparatus used in the measurement of the heat capacity was a precision adiabatic-shield high-vacuum calorimeter suitable for measurements from 15 to 350 K. The apparatus, which has been used by McGee[33], Hwa[21], Ziegler et al.[65], and Liu[31], is similar in design to one described by Scott[52]. A limited description is given below. A more detailed description is given by McGee[33].

A schematic diagram of the calorimeter is given in Figure 1. Briefly the apparatus consists of a copper calorimeter can, G, which contains the sample, surrounded by an adiabatic shield, F. The shield and can are suspended from a guard ring, C. The guard ring is attached to the vacuum jacket, D, and acts as a temperature buffer zone between the bath, B, in which the vacuum jacket is immersed. The vacuum jacket can be evacuated through the monel tubing, A, or helium gas can be introduced to the jacket to facilitate the cooling of the sample.

The calorimeter has three basic electrical circuits. These are: (1) the circuit controlling the temperature of the adiabatic shield and guard ring, (2) the circuit controlling the energy input to the calorimeter can, and (3) the circuit to measure the equilibrium temperature of the calorimeter can.

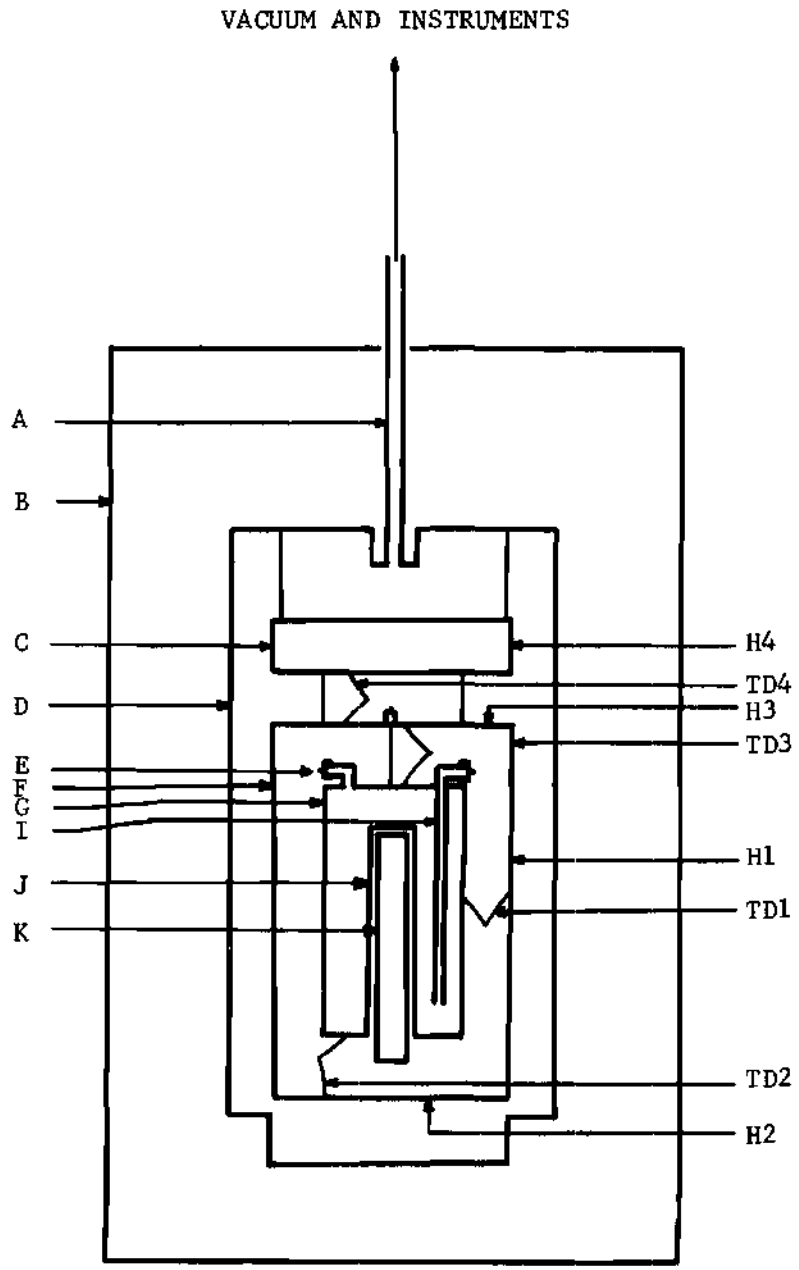


**Figure 1.** Schematic Diagram of Calorimeter.

The temperature difference between the adiabatic shield and calorimeter can was monitored with 3 three-junction constantan-chromel-P thermocouples, TD1, TD2, TD3. The temperature of the shield was controlled with three electrical heaters, H1, H2, and H3. All electrical leads were wound around the ring, C, before passing through the monel tubing, A. Therefore the temperature difference between the ring and the adiabatic shield was monitored with thermocouple, TD4, and the temperature of the ring was adjusted with an electrical heater, H4. During an equilibrium period or an energy input period the shields could easily be maintained within a temperature difference of less than 0.01 degrees with respect to G.

A variable temperature bath was used by Hwa[21]. However, McGee[33] and Liu[31] used constant temperature baths for specific temperature ranges in their work. Constant temperature baths were used in the present work. For this reason, a drift rate study was initiated to determine the effect of the baths on the heat capacity measurements. The drift rate study is summarized in Appendix F. The result of the study was that shield control using the constant temperature baths had a maximum effect on the heat capacity of less than 0.1 per cent.

The energy input circuit is shown schematically in Figure 10, Appendix D. The energy input to the calorimeter heater, J, was determined by measuring the voltage across and the current flowing thru the heater with a 100,000 microvolt White double potentiometer. The voltage was supplied by a constant voltage D.C. power supply (Hewlett-Packard Model 6101A). The power supply provided a voltage difference accurate to 0.001 per cent with a variation of the current in the

curcuit by less than 0.00001 per cent. The standard resistor, the standard cells, and the volt box in the circuit were calibrated by the U.S. National Bureau of Standards. The time of a heat input was determined with a 110 volt, 60 cycle type S-10 electric timer (Standard Electric Timer Company). A previous analysis[33] showed the heating interval could be determined to within 0.1 second.

The temperature measurements were made with a platinum resistance thermometer, K, made by the Leeds and Northrup Company. The thermometer (Leeds and Northrup No. 1048215) was calibrated by the U.S. National Bureau of Standards on the International Practical Temperature Scale of 1948 down to the normal boiling point of oxygen, -182.970 C. The resistance of the thermometer was measured with a Leeds and Northrup Mueller G-2 resistance bridge to better than 0.0001 ohm (0.001 C).

## Experimental Procedure

There were four steps involved in the experimental procedure of preparing the sample for a heat capacity measurement: (1) the preparation of a mixture, (2) the transfer of the mixture or pure component to the calorimeter can, (3) the sealing of the sample in the calorimeter can, and (4) the sealing of the calorimeter can in the adiabatic calorimeter.

To prepare a mixture, a precision Mettler balance was used to weigh the pure components of the mixture. A specially made weighing bottle having a marked volume of 170 ml. and weighing 30 gms. was used to transfer the pure components to a reagent bottle. The reagent bottle

had previously been cleaned and vacuum dried. This procedure afforded a rough check on the amount of pure component used to make the mixture.

One hundred seventy milliliters of sample were transferred to the weighing bottle. All transfers were made using dry gaseous nitrogen. Once the weighing bottle plus sample was weighed, then the sample was transferred to the calorimeter can, which had been cleaned and vacuum dried for at least 30 minutes. The empty calorimeter can, which weighs approximately 193.6 gms. and has a volume of 160 ml., was filled to about 10 ml. of its capacity. The weight of the sample (approximately 110 gms.) was determined on a rough balance to 0.02 gm. from the total weight of the can (approximately 300 gms.). A check on the weight of the sample was possible from the differences in the weight of the weighing bulb plus sample.

The calorimeter can was sealed by soldering two brass caps, E, on the entrant tubes, E and I, with 50-50 tin lead solder. The amount of solder added never varied by more than 0.02 gram. This variation was shown to have a negligible effect on the measured heat capacity in Appendix D.

The calorimeter can was suspended in the calorimeter. All leads were connected and tested for electrical grounding and shorts. The adiabatic shield was replaced. The vacuum jacket was soldered using 40-60 tin lead solder and tested for vacuum tightness. The calorimeter was evacuated to $10^{-5}$ torr. The system was ready for heat capacity measurements.

The calorimeter can and sample were cooled to the desired temperature with helium as the heat exchange gas. An ice bath was used

for the temperature range 0 to 35°C, a dry ice-ethanol bath for -78 to 0°C, and a liquid nitrogen bath for temperatures below -78°C.

The heat capacity measurements involved five steps: 1) the balancing of the temperature of the ring, adiabatic shield, and the calorimeter can, 2) the measurement of the initial resistance of the platinum resistance thermometer, 3) the measurement of the potential across the standard resistor and across the volt box (from which the potential across the heater can be determined), 4) the measurements of the total time that energy was supplied to the can, and 5) the measurement of the final resistance of the platinum resistance thermometer.

Heat capacity measurements were made continuously when possible, i.e. the final temperature of one measurement was the initial temperature for the next measurement. The temperature interval used was four to five degrees with time intervals of 900 to 1400 seconds.

# CHAPTER III

## EXPERIMENTAL RESULTS AND DISCUSSION

The raw calorimetric data, taken during a heat capacity measurement, (1) thermometer resistances, (2) potential across the heater, (3) potential across the standard resistor, and (4) the time of an energy input, were used to calculate the heat capacity of the sample. The molar heat capacity was then calculated from the mass of the sample. The calculations were processed on a Burroughs 5500 digital computer. A sample calculation is given in Appendix D. Numerical constants and the temperature scale and energy conversions used in all calculations are given in Appendix A.

A heat capacity measurement was composed of four parts: (1) the heat capacity of the sample, (2) the heat necessary to vaporize part of the sample, (3) the heat capacity of the gas phase above the liquid, and (4) the heat capacity of the calorimeter can. The effects of (2) and (3) are shown to be negligible in Appendix D and are neglected. The heat capacity of the can had been determined by Hwa[21], who fitted a fourth degree polynomial in temperature to his data (Appendix D). The heat capacity of the can was calculated from the polynomial at the midpoint of the heat capacity measurement. The heat capacity of a sample was the total heat capacity minus the heat capacity of the can.

The calorimeter can was sealed at room temperature under an atmosphere of essentially dry gaseous nitrogen. A calculation was made, that indicated the difference between the measured quantity, $C_{sat}$, and

Cp, was negligible for the range of temperature in this work. Therefore the measurements are taken to give Cp.

The molar heat capacity of each of the pure components was determined by the above method. These data are given in Tables 6, 7, and 8 of Appendix B. The heat capacity data were fitted by a polynomial in temperature by the method of least squares. The polynomials are given in Table 11 on the International Practical Temperature Scale of 1968 (IPTS-68) and Table 12 of Appendix B on the International Practical Kelvin Scale of 1954 (IPKS-54).

The molar heat capacity of each mixture, $C_p^s$, was determined by the same method. From the polynomial mentioned above, the heat capacities of the pure components, $C_{pi}^o$, were evaluated at the midpoint of the temperature of the $C_p^s$ measurement. The excess heat capacity, $C_p^E$, was calculated from its definition, Equation (6), Chapter IV. The midpoint temperature of the $C_p^s$ measurement was assigned to the $C_p^E$ value. The excess heat capacity data for each mixture were fitted by a polynomial in temperature by method of least squares. The $C_p^s$ and $C_p^E$ data are given in Tables 9 and 10 of Appendix B. The polynomials are given in Table 11 of Appendix B.

The heat capacity data measured are summarized in Table 1. The heat capacity data of n-heptane, 2-propanol, and ethanol are given in Tables 6, 7, and 8 respectively of Appendix B. The heat capacity data and the excess heat capacity data of the 2-propanol + n-heptane system are given in Table 9, Appendix B. The heat capacity data and the excess heat data of the ethanol + n-heptane system are given in Table 10, Appendix B.

Table 1. Summary of the Heat Capacity Measurements.

| Sample | Mole Fraction of Alcohol | Temperature Range, K |
|---|---|---|
| n-Heptane | | Melting Point to 302 |
| 2-Propanol | | Melting Point to 304 |
| Ethanol | | Melting Point to 306 |
| 2-Propanol + n-Heptane | 0.4219* | 187 to 305 |
| | 0.5993 | 188 to 305 |
| | 0.0809 | 188 to 304 |
| | 0.7984 | 188 to 305 |
| | 0.2492 | 188 to 304 |
| Ethanol + n-Heptane | 0.8107 | 203 to 306 |
| | 0.6140 | 219 to 306 |
| | 0.2805 | 216 to 306 |
| | 0.1023 | 212 to 305 |
| | 0.4388 | 195 to 305 |

* Compositions are given in chronological order of measurement.

The heat capacity data for n-heptane, 2-propanol, and ethanol were fitted by fifth, third, and fourth degree polynomials in temperature, respectively. The polynomials fit the data with an average deviation of 0.06 Joules/gm. mole-K and a maximum deviation of 0.40 Joules/mole-K. The excess heat capacity data of the 2-propanol + n-heptane system were fitted by a fourth degree polynomial for each mixture. The average deviation of the fit from the experimental data was 0.04 Joules/mole-K and a maximum deviation of 0.16 Joules/mole-K. The excess heat capacity data of the ethanol + n-heptane system were fitted by a fourth degree polynomial for each mixture. The average deviation of the fit from the experimental data was 0.04 Joules/mole-K and the maximum deviation was 0.21 Joules/mole-K.

The melting points and purity of the pure components were found calorimetrically. A more complete discussion of the method and of the results are given in Appendix E. The melting points were measured to be 158.991, 185.232, and 182.565 K for ethanol, 2-propanol, and n-heptane, respectively. These results on the IPKS-54 are compared to literature values in Table 24, Appendix E. The purities calculated from the melting point experiments are 99.94, 99.84, and 99.70 mole per cent for ethanol, 2-propanol, and n-heptane, respectively (Table 23, Appendix E).

Andon et al.[1] have measured the heat capacity of 2-propanol. The standard deviation of their work from their smoothed data was given as 0.1 per cent. A comparison of the smoothed heat capacity of the present work with their experimental data gave an average deviation of 0.03 cal./mole, or 0.11 per cent, and a maximum deviation of 0.33 per cent. The comparison of data is given in Table 13, Appendix B.

The heat capacity of ethanol has been measured by Hwa[21], by Nikolaev et al.[36], and by Kelley[24]. Kelley stated that above 200 K heat capacities may be in error by as much as 1 per cent. Nikolaev et al. stated an accuracy of 0.2 per cent. However, both sets of measurements deviate from the present work with a maximum deviation slightly larger than one per cent. The measurements of Hwa deviate from the present measurements by an average deviation of 0.16 per cent. Hwa failed to make a buoyancy correction in the calculation of the weight of his sample. This discrepancy accounts for a systematic 0.13 per cent deviation. With this correction the measurements of Hwa

and the present work are in excellent agreement with each other. The comparison of data with Hwa is given in Table 14, Appendix B. The measurements of the heat capacity of ethanol made in this laboratory appear to be the best set of data available in the literature.

The heat capacity of n-heptane has been measured by the U.S. National Bureau of Standards[10] and by the U.S. Bureau of Mines[34]. Both groups worked with n-heptane which had a purity of 99.97 per cent. McCullough and Messerly[34] made an analysis of the five sets of measurements of the Bureau of Mines. From their analysis they selected what they considered to be the most probably heat capacities. They compared these selected heat capacities with the U.S. National Bureau of Standards measurements, which were consistently low by an average deviation of 0.04 cal./mole-K, or 0.1 per cent. The smoothed results of the measurements of the present work are consistently low by 0.09 cal./mole-K, or 0.2 per cent with a maximum deviation of 0.24 per cent. The impurity of the n-heptane was estimated to account for a large part of this discrepancy. However, taken overall, the results agree well within experimental error. The comparison of the data is given in Table 15, Appendix B.

The excess heat capacity of the 2-propanol + n-heptane system has not been previously determined. The excess heat capacity data of the ethanol + n-heptane system have been determined by Klesper[26] from 20 to 70°C. The accuracy of his work was given as 0.07 per cent of the heat capacity or 0.15 to 0.07 Joule/mole-K uncertainty in the excess heat capacity from pure ethanol to pure n-heptane, respectively.

The accuracy claimed in the present work is 0.15 to 0.07 Joule/mole-K. The two results deviate by about 0.5 Joule/mole-K. A comparison of the two works showed the heat capacity of n-heptane agreed within 0.03 per cent, but the heat capacity of ethanol deviated by as much as 0.8 per cent. Klesper did not give the purity of the ethanol, so presumably the impurity was significant enough to cause the discrepancy between his work and the present work.

In view of the reproducibility of the heat capacities, of the average deviations and maximum deviations from smoothed data, and of the agreement with data available in the literature, it is concluded that the heat capacities of the pure components and mixtures are accurate to 0.2 per cent. The error in the excess heat capacity is related to the reproducibility of the heat capacity measurement. The reason for this is that even though a systematic error might be present resulting in a large absolute error in the heat capacity, this systematic error would tend to cancel out in the determination of the excess heat capacity. Since the reproducibility of the heat capacity data is a random error, the error in $C_p^E$ is the sum of the error in $C_p^s$ and $C_{p_i}^o$ times the square root of two. On this basis the excess heat capacity is estimated to be accurate to 0.15 to 0.07 Joule/mole-K from pure n-heptane to pure alcohol respectively.

# CHAPTER IV

## EXCESS THERMODYNAMIC PROPERTIES OF ETHANOL + n-HEPTANE AND 2-PROPANOL n-HEPTANE SYSTEMS

### Determination of Thermodynamic Relations

The excess thermodynamic properties are a measure of the deviation of a solution from ideal behavior. The definition of an excess property at the temperature and vapor pressure of the solution is

$$X^E = X^S - \sum_j x_j X_j^O = \Delta X^M - (\Delta X^M)^{id} \qquad (1)$$

where $X^S$ = molar value of property of the solution

$x_j$ = mole fraction of component j

$X_j^O$ = molar value of pure j at T, P of solution.

If the property X is heat capacity, enthalpy, entropy, or Gibbs free energy then

$$C_p^E = C_p^S - \sum_j x_j C_{pj}^O = \Delta C_p^M \qquad (2)$$

$$H^E = H^S - \sum_j x_j H_j^O = \Delta H^M \qquad (3)$$

$$S^E = S^S - \sum_j x_j S_j^O + R \sum_j x_j \operatorname{Ln} x_j = \Delta S^M + R \sum_j x_j \operatorname{Ln} x_i \qquad (4)$$

$$G^E = G^S - \sum_j x_j G_j^O - R \cdot T \sum_j x_j \operatorname{Ln} x_j = \Delta G^M - R \cdot T \sum_j x_j \operatorname{Ln} x_j \; . \qquad (5)$$

The properties are interrelated by thermodynamic relations. In the present work the excess heat capacity is determined from the heat capacity of the pure components and of the mixture. For this reason, the other properties are expressed in terms of the excess heat capacity in the following mathematical relations

$$\left(\frac{\partial H^E}{\partial T}\right)_{p,x} = C_p^E \tag{6}$$

$$\left(\frac{\partial S^E}{\partial T}\right)_{p,x} = \frac{C_p^E}{T} \tag{7}$$

$$G^E = H^E - T S^E . \tag{8}$$

The effect of the change of pressure ($p \leq$ latm.) on the excess properties is shown to be negligible in Appendix G; therefore the data can be taken as at constant pressure. Once $C_p^E$ has been determined as a function of temperature, then the properties $H^E$, $G^E$, and $S^E$ can be determined as a function of temperature once the integration constants $H^E$ and $G^E$ are known at a fixed temperature, by integrating, Equations (6), (7), and (8). The excess heat capacity is presented as a function of temperature in polynomial form in Table 11, Appendix B.

The activity coefficients are determined from a compositional fit of the excess Gibbs free energy at a fixed temperature. The derived excess Gibbs free energy data are fitted with the Redlich-Kister equation,[35] the modified Redlich-Kister equation,[35] the Wilson equation,[64] and the Wiehe-Bagley equation[62] by the method of least squares. The activity coefficients are calculated from the excess Gibbs free energy

functions with the relations

$$R \cdot T \ \mathrm{Ln} \ \gamma_a = G^E + x_h \left(\frac{\partial G^E}{\partial x_a}\right)_{P,T} \tag{9}$$

$$R \cdot T \ \mathrm{Ln} \ \gamma_h = G^E - x_a \left(\frac{\partial G^E}{\partial x_a}\right)_{P,T} \tag{10}$$

and the parameters in Tables 29, 33, and 34, Appendix H. The activity coefficients are given in Tables 37, and 38, Appendix H for the ethanol + n-heptane and 2-propanol + n-heptane systems, respectively.

## Literature Data Used

The integration constants needed to integrate Equations (6) and (7) are available in the literature. For the 2-propanol + n-heptane system Van Ness et al.[54,59] have measured the excess enthalpy from 303.15 to 333.15 K and vapor-liquid equilibrium data at 303.15 K. They also extracted the excess Gibbs free energy from vapor-liquid equilibrium measurements. The $H^E$ and $G^E$ data at 303.15 K were used as integration constants.

The ethanol + n-heptane system has been thoroughly studied near room temperature. The excess enthalpy has been measured by Van Ness et al.[27,60] from 283.15 to 348.15 K, by Grosse-Wortman et al.[15] at 293.15 K, and by Ramalho et al.[42] from 293.15 to 303.15 K. Klesper[26] used his determination of the excess heat capacity from 293.15 to 343.15 K and the excess enthalpy of Grosse-Wortmann to derive $H^E$ at 303.15 K. The excess enthalpy data all agreed within experimental error. The excess Gibbs free energy data have been determined by Van Ness et al.[27,60]

at 303.15 K and by Rothe[48] from 303.15 to 333.15 K from their vapor-liquid equilibrium measurements.

The excess enthalpy and excess Gibbs free energy data of Van Ness et al. are used for the ethanol + n-heptane system. The reasons for using their data are to get internal consistency and that they made very extensive measurements as a function of composition. The data for both systems were smoothed graphically for the purpose of interpolation and are given in Tables 16 and 17, Appendix C.

## Results and Discussion

The excess enthalpy, excess Gibbs free energy, and excess entropy are derived from the excess heat capacity data of the 2-propanol + n-heptane and ethanol + n-heptane systems. For 2-propanol + n-heptane the excess properties are derived from 183.15 to 303.15 K at five degree intervals. For the ethanol + n-heptane system the excess properties are derived from 213.15 to 303.15 K at five degree intervals. The excess properties are given in Table 17, Appendix C. All quantities outside these temperature ranges were obtained from an extrapolation of the functional representation of the excess heat capacity as given in Table 11, Appendix B. The Gibbs free energy of mixing is also derived and given in Tables 18 and 19, Appendix C. The temperature and composition behavior for $C_p^E$, $H^E$, $G^E$, and $S^E$ is shown in Figures 2, 3, 4, and 5, respectively.

The activity coefficients for ethanol + n-heptane are derived at 213.15, 243.15, 273.15, and 303.15 K and are given in Table 37, Appendix H. The activity coefficients for 2-propanol + n-heptane are

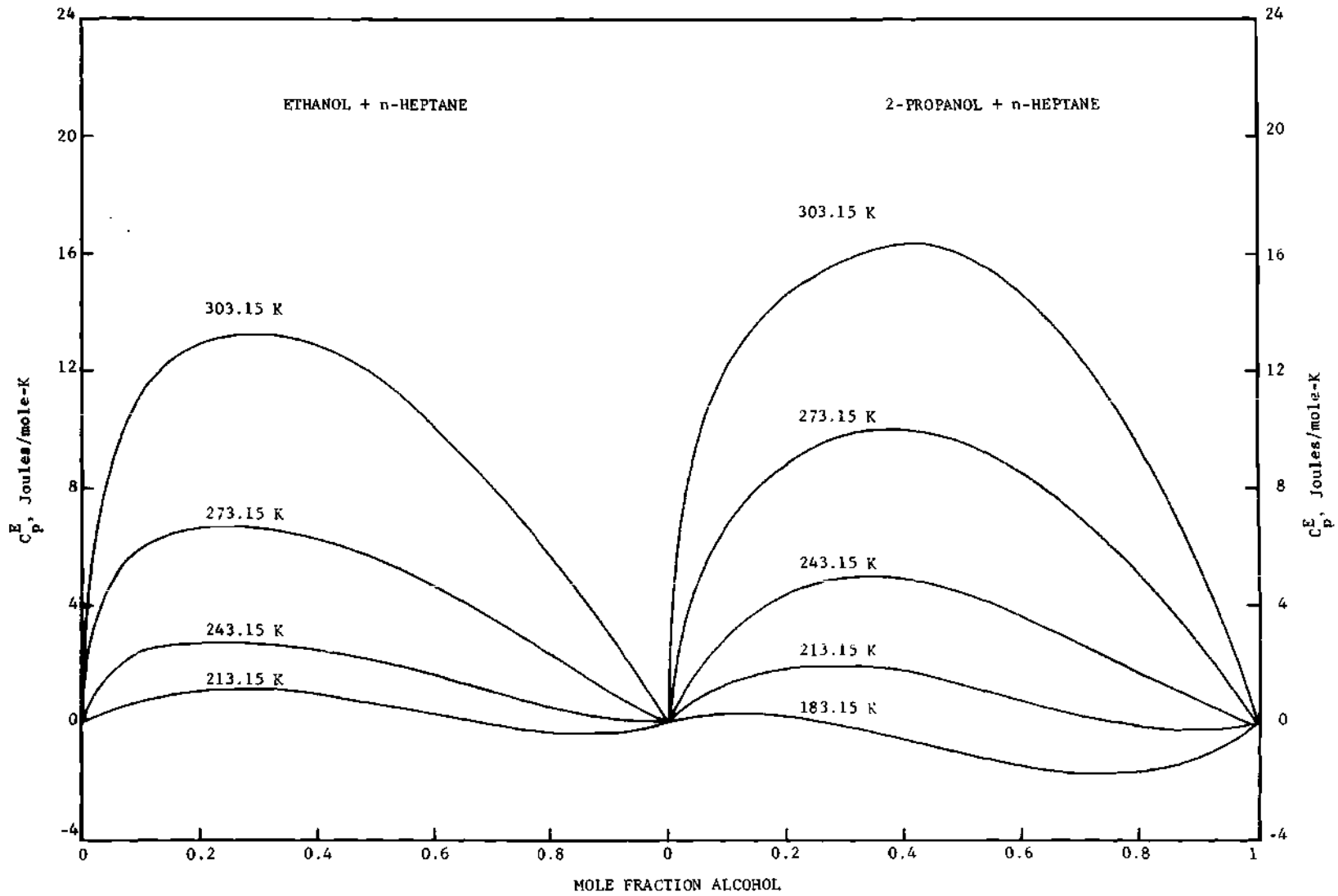


Figure 2. Excess Heat Capacity as a Function of Temperature and Composition.

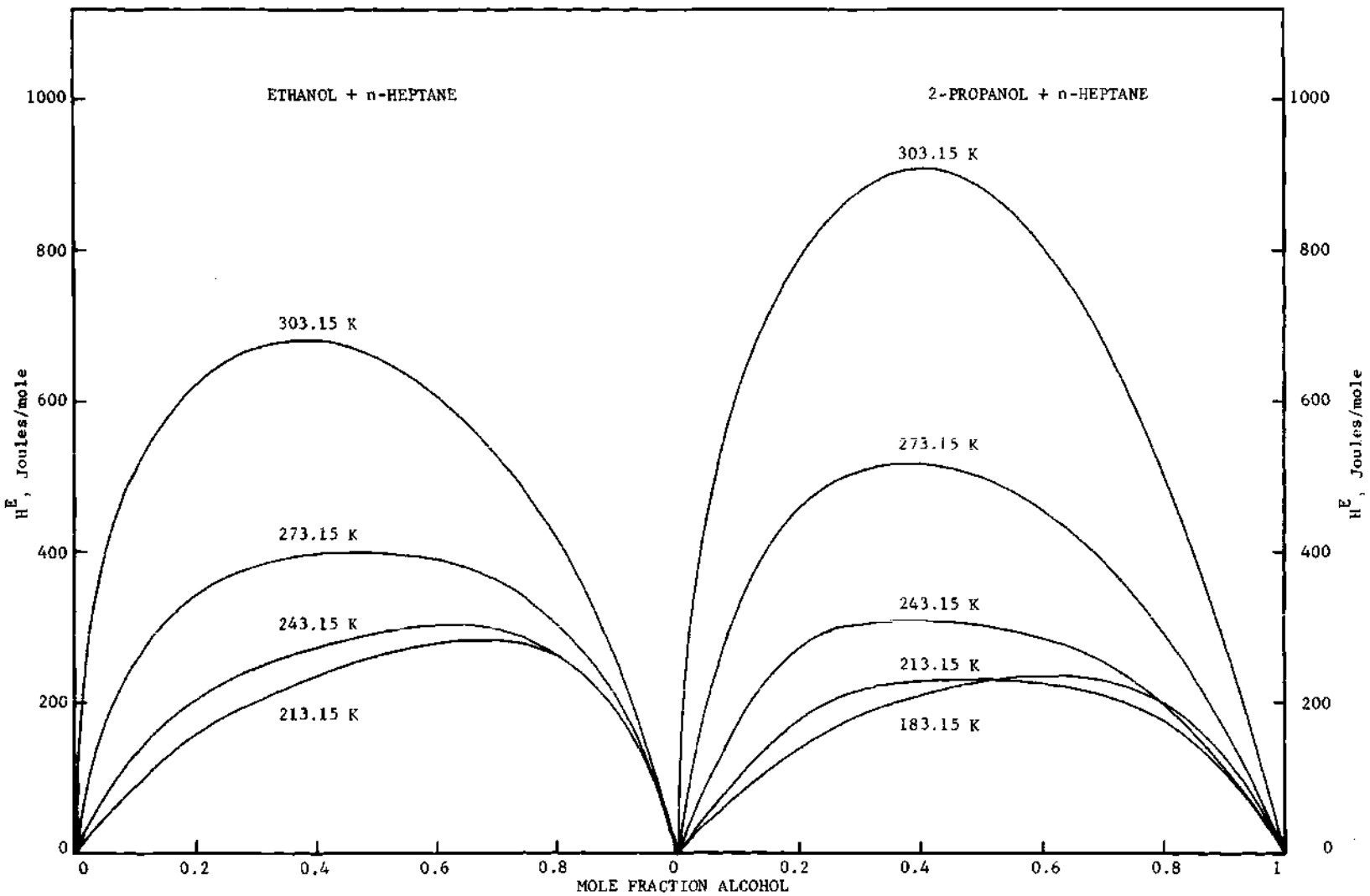


Figure 3. Excess Enthalpy as a Function of Temperature and Composition.

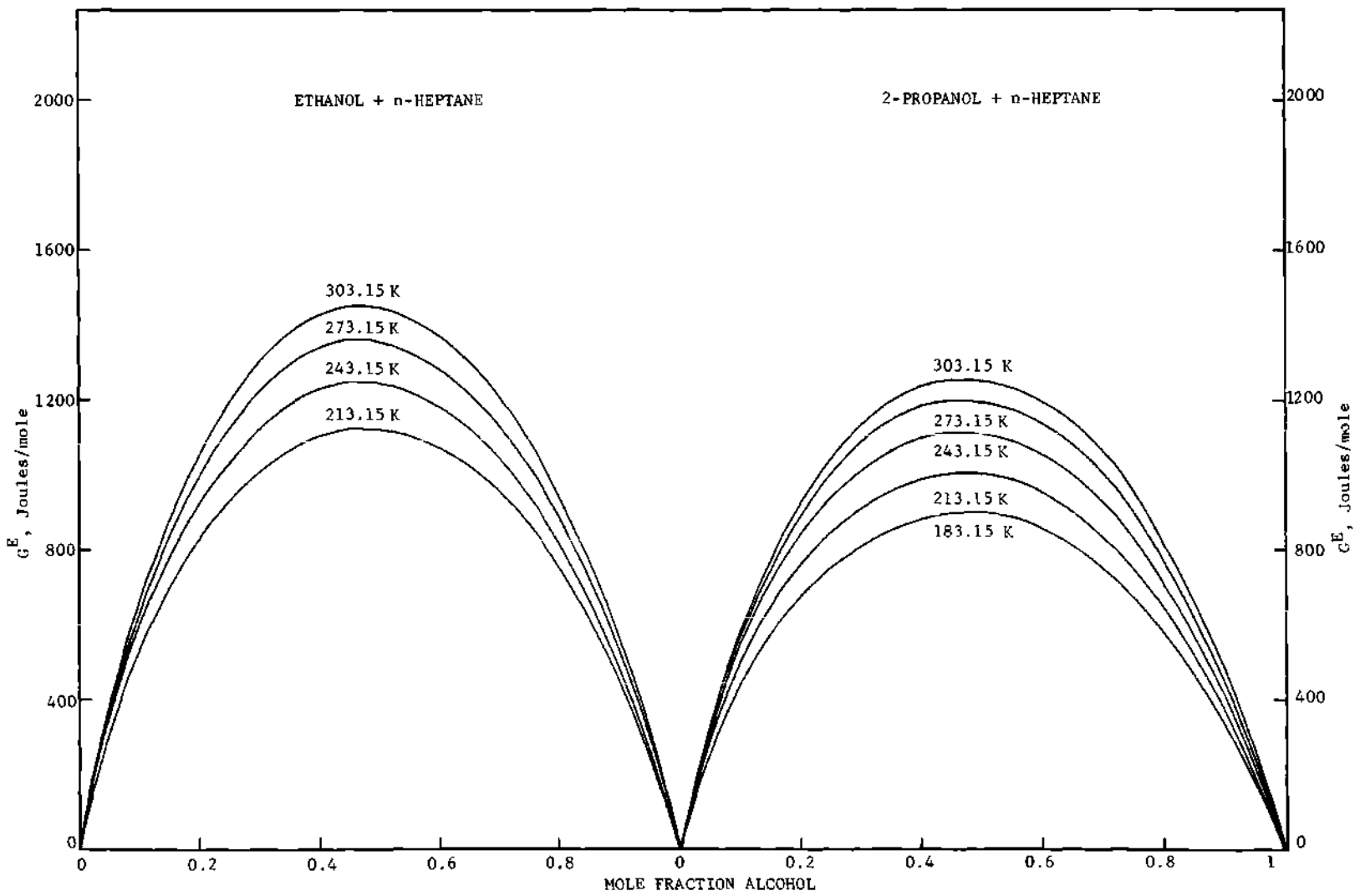


Figure 4. Excess Gibbs Free Energy as a Function of Temperature and Composition.

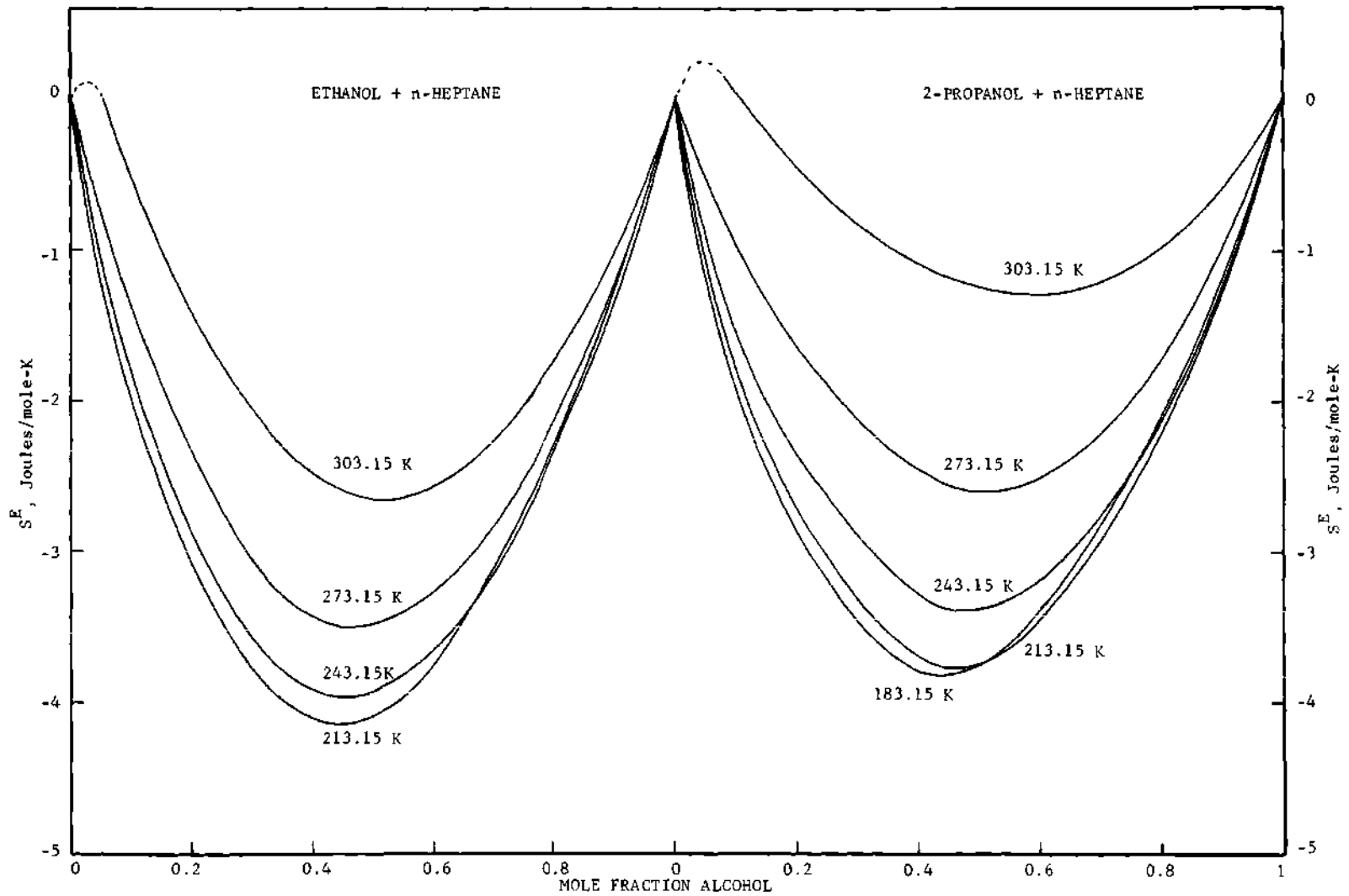


Figure 5. Excess Entropy as a Function of Temperature and Composition.

derived at 183.15, 213.15, 243.15, 273.15, and 303.15 K and are given in Table 38, Appendix H.

The excess enthalpy data for ethanol + n-heptane at 293.15 K in the present work agree with the measurements of Grosse-Wortmann et al[15] and Ramalho and Ruel[42] within better than two per cent. The excess enthalpy data for ethanol + n-heptane derived at 283.15 K in the present work also agree with the measurements of Van Ness et al.[27,60] within better than two per cent. The excess heat capacity data for the ethanol + n-heptane and 2-propanol + n-heptane systems are extrapolated to derive the excess enthalpy for both systems at 318.15 K. The excess enthalpy for both systems agrees with the data of Van Ness et al.[27,60] to within better than two percent. The agreement of the derived excess enthalpy data with experimental measurements gives an indication of the accuracy of the excess heat capacity data.

The uncertainty in the derived excess thermodynamic properties arises from two sources: the uncertainty in the integration constants and the error due to the integration of the excess heat capacity data. The first error is a constant error (i.e., an error of 10 Joules/mole in $H^E$, $S^E$, or $G^E$ at 303.15 K is transmitted as an error of 10 Joules/mole in $H^E$, $S^E$, or $G^E$ at 213.15 K). The second error is propagated with temperature and is the product of the error in the excess heat capacity and the temperature difference. The error in the excess heat capacity (see Chapter III) is 0.15 to 0.07 Joules/mole-K from a concentration of pure n-heptane to pure alcohol respectively. The uncertainty in the excess enthalpy taken from the literature is estimated

to be one to two per cent. The uncertainty of the excess Gibbs free energy data taken from the literature is estimated to be two per cent in light of the absence of experimental second interaction virial coefficient data and the uncertainty of the experimental data. An error analysis yielded an uncertainty in the excess enthalpy of 4 to 12 Joules/gm. mole at 303.15 K increasing to 17 to 26 Joules/gm. mole at 183.15 K. The error analysis yielded an uncertainty in the excess Gibbs free energy of 2 to 7 Joules/gm. mole at 303.15 K. increasing to 6 to 13 Joules/gm. mole at 183.15 K. The uncertainty of the excess entropy is 0.02 to 0.06 Joules/gm. mole-K at 303.15 increasing to 0.16 Joules/gm. mole-K at 183.15 K. An error analysis is not made for the activity coefficients. However, they are derived by three different methods, thus giving an indication of the maximum errors.

The excess thermodynamic properties of the alcohol-hydrocarbon systems have mostly been studied at and above room temperature. Ethanol + n-heptane and 2-propanol + n-heptane represent the behavior of these systems in this temperature range as shown in Figures 2, 3, 4, and 5 at 303.15 K. The excess heat capacity versus temperature curve has a positive slope, indicating the excess enthalpy increases with increasing temperature. The excess enthalpy is large, positive, and has a maximum in the dilute alcohol concentration region near room temperature. The excess entropy is negative except at low alcohol concentrations where the entropy becomes positive. The minimum of the excess entropy is in the alcohol rich region. The excess enthalpy and excess entropy compensate to give an excess Gibbs free energy which has its maximum near

the equimolar composition and is large and positive.

Rowlinson[49] gives an explanation for the general behavior of an alcohol in a non-polar solvent near room temperature. The three points emphasized by Rowlinson are

(1) The majority of the excess enthalpy is a measure of the number of hydrogen bonds and other local electrostatic interactions that are broken on forming a mixture with an inert solvent. The excess enthalpy is small in mixtures rich in alcohol since the addition of a small amount of an inert solvent breaks few hydrogen bonds. The inert solvent is probably accommodated interstitially in a matrix of hydrogen bonded alcohol molecules. The excess enthalpy is large in mixtures weak in alcohol, since the addition of a small amount of alcohol to a large amount of the inert solvent must necessarily break the majority of the hydrogen bonds.

(2) The excess entropy is positive in mixtures very dilute in alcohol due to the loss of orientational order that necessarily follows the breaking of all of the hydrogen bonds. The excess entropy becomes negative with increasing concentration of alcohol, since the mixture now contains a number of hydrogen bonds. The hydrogen bonds impose both a positional and orientational order on the system that is greater than that to be expected in a randomly dispersed solution. This accounts for the asymmetry of the excess entropy with a minimum in the alcohol rich region.

(3) The opposite signs of the excess enthalpy and excess entropy are roughly explained in that no hydrogen bonds broken corresponds to a zero heat of mixing and very few hydrogen bonds remaining

corresponds to zero excess entropy. The real system departure from these hypothetical states lead to the sign and asymmetry observed for the excess enthalpy and excess entropy. The complementary asymmetry of these two functions lead to the symmetrical excess Gibbs free energy.

The behavior of ethanol + n-heptane and 2-propanol + n-heptane near and above room temperature is explained by Rowlinson's three points. The behavior of the excess thermodynamic properties at lower temperatures is different from the behavior at and above room temperature for ethanol + n-heptane and 2-propanol + n-heptane. The behavior of the alcohol-hydrocarbon systems as a function of temperature, which has been examined in the present work at lower temperatures, is now discussed.

The excess thermodynamic properties and their temperature dependence for ethanol + n-heptane can be described as follows: (1) the excess enthalpy is large and positive, decreases with decreasing temperature except at low temperatures in the alcohol rich concentration region, and has a shift of the maximum from the dilute alcohol range to the alcohol rich range as the temperature decreases, (2) the excess entropy is negative except in the dilute alcohol concentration range, becomes more negative with decreasing temperature, and has a shift of the minimum from the alcohol rich range to the dilute alcohol rich range as the temperature decreases, and (3) the excess Gibbs free energy is large and positive, decreases with decreasing temperature, and has a maximum near the the equimolar composition at all temperatures.

The excess thermodynamic properties and their temperature

dependence for 2-propanol + n-heptane are similar to those of ethanol + n-heptane. The 2-propanol + n-heptane system differs in the following respects: (1) the excess enthalpy is larger near room temperature but approximately the same as ethanol + n-heptane at the lowest temperature, (2) the excess entropy is less negative near room temperature but approximately the same as ethanol + n-heptane at the lowest temperature, and (3) the excess Gibbs free energy is smaller.

The temperature dependence of the excess properties at temperatures above and below room temperature is similar. The deviations of behavior below room temperature for the two alcohol-hydrocarbon systems have been discussed above. An interpretation of the excess property data below room temperature is now presented. The decrease of excess enthalpy with temperature can be interpreted as the decrease in the number of hydrogen bonds broken. Fewer hydrogen bonds broken results in more order and also explains the more negative excess entropy. The shift of the maximum of the excess enthalpy from the dilute alcohol to the alcohol rich concentration region can be explained by an increasing average chain length of alcohol polymers with decreasing temperature. In other words the number of actual moles present are fewer than is indicated by the stoichiometric composition. At lower temperatures the excess enthalpy and excess entropy are almost independent of temperature. The non-ideality arising from dispersion force interactions generally increases moderately with decreasing temperature. The variation with temperature of the excess enthalpy and excess entropy at lower temperatures is interpreted as being due to the contribution

from the breaking of hydrogen bonds decreasing at such a rate as to approximately cancel the increase of the contribution from the dispersion force interaction.

A correlation of the excess Gibbs free energy was made with the Redlich-Kister equation[35], a modified Redlich-Kister equation[35], the Wilson equation[64], and the Wiehe-Bagley equation[62] for ethanol + n-heptane and 2-propanol + n-heptane. The results of the analysis is given in more detail in Appendix H. The activity coefficients are calculated using Equations (9) and (10) in conjunction with the Redlich-Kister, Wilson, or Wiehe-Bagley equation. Explicit relations for the activity coefficients are given in the literature[62]. The activity coefficients are obtained for ethanol + n-heptane and 2-propanol + n-heptane. The results of these calculations are given in Appendix H.

The first three of the above mentioned equations are of an empirical nature in which the parameters have very little physical significance. Orye and Prausnitz[37] have, however, given a qualitative significance to the parameters of the Wilson equation. The parameters of the Wiehe-Bagley equation do have physical significance.

The results of the empirical correlations were that the excess Gibbs free energy could be represented as a function of composition (above 0.08 mole fraction alcohol) at each isotherm (from 183.15 to 303.15 K). The Redlich-Kister equation, the modified Redlich-Kister equation, and the Wilson equation gave average deviations of less than 0.5 per cent and maximum deviations of less than 0.8 per cent at each isotherm of the ethanol + n-heptane system. For the 2-propanol +

n-heptane system average deviations are less than 0.5 per cent for the two forms of the Redlich-Kister equation but average deviations are as large as 2 per cent for the Wilson equation. However, for both systems the Wilson equation is able to correlate the data with the fewest number of parameters (two) and for this reason is preferable for correlation of the $G^E$ data. A more extensive discussion of the correlations is given in Appendix H.

The qualitative results obtained earlier will now be discussed in light of the results of the correlation of the $G^E$ data with the Wiehe-Bagley equation. The excess Gibbs free energy data were correlated reasonably well by the Wiehe-Bagley equation with average deviations as large as 13 per cent at 183.15 K for the 2-propanol system. The activity coefficients obtained for 2-propanol + n-heptane indicate that the Wiehe-Bagley equation gives a better representation of the data near room temperature than at lower temperatures. This conclusion is based on comparison with activity coefficients of Van Ness et al.[60] from experimental vapor-liquid data at 303.15 K and the seemingly unreasonably large activity coefficients calculated from the Wiehe-Bagley equation at the lowest temperature. The parameters were determined solely from the excess Gibbs free energy data.

The excess enthalpy was calculated by differentiation of the $G^E$ data since

$$H^E = - T^2 \frac{\partial (G^E/T)_{p,x}}{\partial T} \quad . \tag{11}$$

The excess enthalpy calculated by this procedure from the parameters (Table 34) of the Wiehe-Bagley equation is given in Tables 2 and 3. The predicted excess enthalpy also represents the general behavior that the alcohol-hydrocarbon systems exhibit, namely that:

(1) The excess enthalpy is large, positive, and decreases with decreasing temperature.

(2) The excess enthalpy has a maximum in the dilute alcohol mole fraction region near room temperature shifting to the alcohol rich mole fraction region at lower temperatures.

All of the activity coefficient data (Tables 37 and 38, Appendix H) increase with decreasing temperature. This suggests the possibility of phase separation, although the thermodynamic condition for phase separation is that the Gibbs free energy of mixing versus composition exhibits a common slope at different compositions of an isotherm. The Gibbs free energy of mixing data for both alcohol-hydrocarbon systems indicate that phase separation could occur. However, when the error associated with the derived Gibbs free energy of mixing data is considered, phase separation is uncertain for 2-propanol + n-heptane but is certain for ethanol + n-heptane. Qualitative cloud point experiments verify that phase separation does not occur for the 2-propanol system but does occur for the ethanol system at 207.6 $\pm$ 0.5 K for 0.43 mole fraction ethanol. This upper critical solution temperature is very sensitive to the concentration of water.

Table 2. Excess Enthalpy Predicted by the Wiehe-Bagley Equation for Ethanol + n-Heptane.

| | T = 303.15 K | | T = 273.15 K | |
|---|---|---|---|---|
| $x_a$ | $H^E$(W-B)* | $H^E$(Der.)** | $H^E$(W-B)* | $H^E$(Der.)** |
| 0.1023 | 723 | 507 | 371 | 256 |
| 0.2805 | 859 | 664 | 424 | 374 |
| 0.4388 | 778 | 670 | 397 | 399 |
| 0.6140 | 596 | 593 | 329 | 387 |
| 0.8107 | 316 | 408 | 207 | 298 |

| | T = 243.15 K | | T = 213.15 K | |
|---|---|---|---|---|
| $x_a$ | $H^E$(W-B)* | $H^E$(Der.)** | $H^E$(W-B)* | $H^E$(Der.)** |
| 0.1023 | 172 | 136 | 99 | 91.6 |
| 0.2805 | 233 | 242 | 199 | 194 |
| 0.4388 | 260 | 280 | 274 | 239 |
| 0.6140 | 267 | 302 | 335 | 278 |
| 0.8107 | 223 | 260 | 337 | 259 |

* Excess enthalpy predicted by the Wiehe-Bagley equation, Joules/mole. The parameters are given in Table 34, Appendix H.

** Derived excess enthalpy given in Table 17, Appendix C, Joules/mole.

Table 3. Excess Enthalpy Predicted by the Wiehe-Bagley Equation for 2-Propanol + n-Heptane

| | T = 303.15 K | | T = 273.15 K | |
|---|---|---|---|---|
| $x_a$ | $H^E$(W-B)* | $H^E$(Der.)** | $H^E$(W-B)* | $H^E$(Der.)** |
| 0.0809 | 785 | 558 | 445 | 283 |
| 0.2492 | 1069 | 844 | 539 | 490 |
| 0.4219 | 1001 | 910 | 493 | 515 |
| 0.5993 | 785 | 809 | 388 | 460 |
| 0.7984 | 438 | 506 | 234 | 294 |

| | T = 243.15 K | | T = 213.15 K | |
|---|---|---|---|---|
| $x_a$ | $H^E$(W-B)* | $H^E$(Der.)** | $H^E$(W-B)* | $H^E$(Der.)** |
| 0.0809 | 209 | 140 | 95 | 81.3 |
| 0.2492 | 292 | 296 | 181 | 204 |
| 0.4219 | 323 | 296 | 245 | 201 |
| 0.5993 | 315 | 283 | 277 | 222 |
| 0.7984 | 237 | 199 | 241 | 178 |

| | T = 183.15 K | |
|---|---|---|
| $x_a$ | $H^E$(W-B)* | $H^E$(Der.)** |
| 0.0809 | 39 | 59.1 |
| 0.2492 | 98 | 174 |
| 0.4219 | 147 | 187 |
| 0.5993 | 179 | 232 |
| 0.7984 | 168 | 202 |

* Excess enthalpy predicted by the Wiehe-Bagley equation, Joules/mole. The parameters are given in Table 34, Appendix H.

** Derived excess enthalpy given in Table 16, Appendix C, Joules/mole.

# CHAPTER V

# THEORY OF ASSOCIATED SOLUTIONS

## Introduction

A qualitative discussion of the excess thermodynamic properties of ethanol + n-heptane and 2-propanol + n-heptane is given in Chapter IV. A quantitative discussion is given below based on the theory of associated solutions.

The hydrogen bond exists in solutions in which a hydrogen atom is attached to an electronegative atom such as N, F, or O. For this reason the alcohol molecule, R-OH, can form species containing two or more monomer units. The pure alcohol can then be viewed as a mixture of polymer units at chemical equilibrium. The addition of an inert solvent may be viewed as adding one component to the multicomponent analysis.

Based on these ideas, the theory of associated solutions has been developed. The theoretical treatment was first developed by Lassettre[30] and improved by Tobolsky and Blatz[56], Flory[13,14], Redlich and Kister[43], Scatchard[50], Renon and Prausnitz[44], and Haskell et al.[18]. The associated theory has been applied by Redlich and Kister[43], Kretschmer and Wiebe[29], Papousek et al.[38], Tobolsky and Thach[57], Wiehe and Bagley[62], Renon and Prausnitz[44], and Haskell et al.[18] to such solutions. The work which has been done in the field of spectroscopy is reviewed by Pimentel and McClellan[39]. Other recent work that should

be mentioned is that of Van Ness et al.[61], of Dunken and Fritzsche[11], and of Ibbitson and Moore[23], to name a few. Prigogine and Defay[41], Hildebrand and Scott[19], and Prausnitz[40] have reviewed the development of the associated theory.

Two variations of the theory of associated solutions based on the cell model are considered here to explain the temperature and composition behavior of alcohol-hydrocarbon solutions (the size of the hydrocarbon determines the cell size). A volume fraction model, which is derived from volume fraction statistics, is applied to ethanol + n-heptane, 2-propanol + n-heptane, and ethanol + methylcyclohexane. A mole fraction model, which is derived from mole fraction statistics, is applied to ethanol + n-heptane. An excellent discussion of the differences between the two statistical models is given by Haskell et al.[18]. Both statistics assign one cell to the inert solvent molecule. However, volume fraction statistics assign i cells to an i-mer and mole fraction statistics assign one cell to each i-mer. Since the inert solvent varies in size and the i-mer distribution of the alcohol varies in size from one mixture to another, the assignment of cells to a real system would necessarily be expected to lie somewhere between these two extremes.

## Volume Fraction Model

The volume fraction model has been used by other investigators[13,22,29,38,44] to describe the excess thermodynamic functions of the alcohol-hydrocarbon systems. The theoretical development given here closely follows that of Flory[13] and of Renon and Prausnitz[44].

It is assumed that the alcohol in the pure state or in a mixture exists in the form of linear hydrogen bonded polymers and that these polymeric species are formed by reactions, for example

$$R\text{-}OH + (R\text{-}OH)_{i-1} \rightleftarrows (R\text{-}OH)_i \tag{12}$$

where R is some alkyl group. The polymeric species are at chemical equilibrium, therefore

$$\mu_1 + \mu_{i-1} = \mu_i \tag{13}$$

where $\mu_i$ is the chemical potential of what will be referred to as the i-mer (composed of i monomer alcohol species).

Prigogine and Defay[41] show that the partial molar Gibbs free energy of stoichiometric alcohol is equal to the partial molar Gibbs free energy of monomeric alcohol

$$\bar{G}_a = \bar{G}_1 \quad . \tag{14}$$

The excess Gibbs free energy, which is defined by

$$G^E = x_a(\bar{G}_a - G_a^\circ) + x_h(\bar{G}_h - G_h^\circ) - R\,T[x_a \operatorname{Ln} x_a + x_h \operatorname{Ln} x_h] \tag{15}$$

is specified once the quantities $\bar{G}_a$, $G_a^\circ$, $\bar{G}_h$, and $G_h^\circ$ are determined. The lattice model developed by Flory[13] for the thermodynamic properties of solutions of heterogeneous polymers is used to obtain these quantities. Flory develops certain relations for the partial molar free energies. He bases the derivation of these quantities on the

assumptions of 1) a quasi-chemical standard state, 2) the physical interactions between the molecules being characterized by an expression of the van Laar type, and 3) no volume change on mixing. For the monomeric alcohol in a mixture Equation (14) is also used to obtain

$$\bar{G}_a = \bar{G}_1 = G_1^{oo} + R\,T\Big[\mathrm{Ln}\ \Phi_1 - \mathrm{Ln}\ \frac{v_a}{v_h} + \frac{v_a}{v_h}\,\Phi_a - v_a \sum_i \frac{\Phi_i}{v_i}$$

$$- \Big(\frac{v_a}{v_h} - 1\Big)\mathrm{Ln}(\theta - 1) + \mathrm{Ln}\ \tau\Big] + \beta\, v_a\, \Phi_h^2 \quad . \tag{16}$$

For the monomer alcohol in the pure ethanol

$$G_a^o = G_1^o = G_1^{oo} + R\,T\Big[\mathrm{Ln}\ \Phi_i^o - \mathrm{Ln}\ \frac{v_a}{v_h} + \frac{v_a}{v_h} - v_a \sum_i \frac{\Phi_i^o}{v_i}$$

$$- \Big(\frac{v_a}{v_h} - 1\Big)\mathrm{Ln}(\theta - 1) + \mathrm{Ln}\ \tau\Big] . \tag{17}$$

Finally for the solvent

$$\bar{G}_h = G_h^o + R\,T\Big(\mathrm{Ln}\ \Phi_h + \Phi_a - v_h \sum \frac{\Phi_i}{v_i}\Big) + \beta\, v_h\, \Phi_a^2 \quad . \tag{18}$$

In Flory's interpretation of the lattice theory, each cell of the lattice is occupied by a molecule of solvent or by a monomer segment of the i-mer molecule. This idea is used to put the quantity, $v_i$ in the form $i \cdot v_h$. If Equations (16), (17), (18), and the result for the molar volume of an i-mer are substituted into Equation (15), then the expression for the excess Gibbs free energy is obtained

$$G^E = R\,T\left[x_a \,\mathrm{Ln}\,\frac{\Phi_1}{\Phi_1^o x_a} + x_h \,\mathrm{Ln}\,\frac{\Phi_h}{x_h} - \frac{(x_a v_a + x_h v_h)}{v_h}\sum_i \frac{\Phi_i}{i}\right.$$

$$\left. + \frac{x_a v_a}{v_h}\sum_i \frac{\Phi_i^o}{i}\right] + \beta\,\Phi_a \Phi_h (x_a v_a + x_h v_h) \quad . \tag{19}$$

The volume fraction of the polymeric species in solution, $\Phi_i$, of the pure state, $\Phi_i^o$, are unknown quantities in Equation (19). They can be related to the stoichiometric alcohol volume fraction by using the concept of the equilibrium constant for the reaction given in Equation (12)

$$K_i = \frac{\Phi_i}{\Phi_{i-1}\Phi_1}\left[\frac{i-1}{i}\right] \quad . \tag{20}$$

This relation is derived by Renon and Prausnitz[44], and by Flory[13] from the standard Gibbs free energy of formation. It will be assumed that the equilibrium constant is independent of the degree of association (i.e. $K = K_2 = K_3 = \ldots = K_i$). This assumption together with Equation (20) leads to the general expression

$$\Phi_i = (i)\cdot K^{i-1}\cdot \Phi_1^i \tag{21}$$

which relates the volume fraction of the i-mer to the volume fraction of the monomer and to the equilibrium constant. An equation identical to Equation (21) can be derived for the pure alcohol. The two equations are used to put the infinite series, $\sum_i(\Phi_i/i)$ and $\sum_i(\Phi_i^o/i)$, in the closed forms

$$\sum_i \frac{\Phi_i}{i} = \frac{\Phi_1}{(1 - K \cdot \Phi_1)} \qquad (22)$$

for $(K \cdot \Phi_1) < 1$, and

$$\sum_i \frac{\Phi_i^o}{i} = \frac{\Phi_1^o}{(1 - K \cdot \Phi_1^o)} \qquad (23)$$

for $(K \cdot \Phi_1^o) < 1$.

Equations (22) and (23) are combined with Equation (19) to yield

$$G^E = R \cdot T \cdot \left[ x_a \cdot \mathrm{Ln} \frac{\Phi_1}{\Phi_1^o x_a} + x_h \cdot \mathrm{Ln} \frac{\Phi_h}{x_h} + K\, x_a (\Phi_1 - \Phi_1^o) v_a / v_h \right]$$

$$+ \beta \cdot \Phi_a \cdot \Phi_h (x_a \cdot v_a + x_h \cdot v_h) \quad . \qquad (24)$$

This relation is identical* to that given by Renon and Prausnitz[44]. The excess Gibbs free energy is reduced to a function of the parameters $\beta$, which is a physical interaction parameter, and K, which is an equilibrium constant for the associative reaction given in Equation (12). All of the other variables are known quantities or have been

* After the correlation of the excess property data with Equations (24) and (33) had been completed, it was discovered that Prausnitz[40] has examined as an alternate assumption the case $v_i = i \cdot v_a$. This assumption results in relations for $G^E$ and $H^E$ identical with Equation (24) and (33), except that the ratio, $v_a/v_h$, does not appear explicitly. The experimental $G^E$ and $H^E$ data for the ethanol + n-heptane, 2-propanol + n-heptane, and ethanol + methylcyclohexane systems over the complete temperature range studied, were correlated using this modification with the parameters given by Prausnitz[40]. These parameters are: a $H^o$ of -6000 cal/mole (-25104 Joules/mole), and a K at 50°C of 190 for ethanol systems and 60 for 2-propanol systems. It was found that this modification represented the $G^E$ data slightly better than Equation (24), but represented the $H^E$ data less satisfactorily than Equation (33).

related to functions of the equilibrium constant.

The monomer volume fraction can be related to the stoichiometric alcohol volume fraction by a mass balance of alcohol molecules

$$\Phi_a = \sum_i \Phi_i \tag{25}$$

then the infinite series can be put into closed form using Equation (21)

$$\Phi_a = \frac{\Phi_1}{(1 - K\,\Phi_1)^2} \tag{26}$$

for $(K\Phi_1) < 1$. This leads to a quadratic equation in $\Phi_1$ with only one physically significant root

$$\Phi_1 = \frac{1 + 2\cdot K\cdot \Phi_a - \mathrm{SQRT}(1 + 4\cdot K\cdot \Phi_a)}{2\cdot K^2 \Phi_a} \quad . \tag{27}$$

A similar derivation relating the volume fraction of the monomeric alcohol in the pure state to known variables results in

$$\Phi_1^o = \frac{1 + 2\cdot K - \mathrm{SQRT}(1 + 4\cdot K)}{2\cdot K^2} \quad . \tag{28}$$

At this point all of the unknown variables have been related to known quantities.

The excess Gibbs free energy can be expressed as the sum of a chemical contribution and a physical contribution

$$G^E = G_c^E + G_p^E \quad . \tag{29}$$

The physical contribution $G_p^E$ is given by the last term of Equation (24)

$$G_p^E = \beta \cdot \Phi_a \cdot \Phi_h \cdot (x_a \cdot v_a + x_h \cdot v_h) \tag{30}$$

which is given by Scatchard[50]. The chemical contribution is then given by the remainder of Equation (24).

The excess enthalpy can also be expressed as the sum of two contributions, a chemical interaction and a physical interaction. The excess enthalpy is found by differentiating the corresponding excess Gibbs free energy term since

$$\left[\frac{\partial(G^E/R \cdot T)}{\partial T}\right]_{p,x} = - \frac{H^E}{R\,T^2} \quad . \tag{31}$$

The van't Hoff relation is given by

$$\frac{d\ \mathrm{Ln}\ K}{d\ T} = \frac{H^o}{R \cdot T^2} \tag{32}$$

where $H^o$ = molar enthalpy of formation of a hydrogen bond as given by Equation (12). Equations (31) and (32) are used to then differentiate the first term in Equation (24) to obtain the expression for the excess enthalpy due to chemical interaction

$$H_c^E = - K \cdot H^o \cdot \left\{ x_a \cdot (\Phi_1^o/\Phi_1) \cdot \frac{\partial(\Phi_1/\Phi_1^o)}{\partial K} + x_a \cdot (\Phi_1 - \Phi_1^o) \cdot v_a/v_h \right.$$
$$\left. + K \cdot x_a \cdot \left[\frac{\partial \Phi_1}{\partial K} - \frac{\partial \Phi_1^o}{\partial K}\right] \cdot \frac{v_a}{v_h} \right\} \tag{33}$$

and is identical to that given by Renon and Prausnitz[44]. The excess

enthalpy due to physical interactions is obtained by differentiating Equation (30) using Equation (31), letting $\beta$ be temperature dependent

$$H_p^E = \beta' \cdot \Phi_a \cdot \Phi_h \cdot (x_a \cdot v_a + x_h \cdot v_h) \tag{34}$$

where $\beta' = \beta - T(d\,\beta/d\,T)$. The expression for the excess enthalpy is then

$$H^E = H_c^E + H_p^E \quad . \tag{35}$$

The volume fraction model describes both the temperature and composition behavior of an alcohol-hydrocarbon system once $H^o$, K at one temperature, $\beta$, and $\beta'$ have been specified.

## Mole Fraction Model

The mole fraction model has been used by other investigators[18,43] to describe the excess thermodynamic functions of alcohol-hydrocarbon systems. The theoretical development of the model is given by Haskell et al.[18]. The model takes as its starting point the entropy of mixing of an ideal multicomponent system. Based on a disoriented standard state, the model is developed further by letting the chemical reactions, which take place in the actual mixing process, be accounted for by the different mole fractions of the i-mers in the initial unmixed and final mixed states. The model is then simplified by introducing the equilibrium constant for the chemical reaction

$$i(\text{R-OH}) \rightleftarrows (\text{R-OH})_i \tag{36}$$

which is given by

$$k_i = x_i/(x_1)^i \quad . \tag{37}$$

The derivation of Equation (37) is given by Haskell et al. and involves the concept of ideal solutions at equilibrium. Finally the standard free energy of reaction is used to put the relationship for the entropy of mixing in the following form

$$\Delta S^M = -\frac{R}{n}\{n_a \, Ln(x_1^f/x_1^i) + n_h \, Ln \, x_h^f\} + \frac{1}{n_i}\Sigma(n_i^f - n_i^i)h_i^o/T \tag{38}$$

where

$$x_i^f = n_i^f/n^f$$

$$x_i^i = n_i^i/\Sigma_i \, n_i^i$$

$$x_h^f = n_h^f/n^f \quad .$$

As shown by Haskell, et al., the first term is $\Delta G^M/T$ and the second term is $\Delta H^M/T$. The derivation requires the use of $\mu_i = i \cdot \mu_1$ and the definition of the Gibbs free energy of mixing

$$\Delta G^M = G^f - G^i = \frac{1}{n}\Sigma_j \, n_j^f \, \mu_j^f - \frac{1}{n}\Sigma_j \, n_j^i \, \mu_j^i \quad . \tag{39}$$

The excess Gibbs free energy is defined by

$$G^E = \Delta G^M - (\Delta G^M)^{ideal} \quad . \tag{40}$$

It follows that

$$G^E = R \cdot T \cdot \left[ x_a \, \mathrm{Ln}(x_1^f / x_1^i x_a) + x_h \, \mathrm{Ln}(x_h^f / x_h) \right] \tag{41}$$

and

$$H^E = \frac{1}{n} \sum_i (n_i^f - n_i^i) \cdot h_i^c \quad . \tag{42}$$

Equation (41) relates the excess Gibbs free energy to quantities which are known or can be expressed in known quantities. The quantities $x_1^f$ and $x_1^i$ are expressed in terms of known quantities below. Equation (42) has yet to be expressed in terms of known quantities.

An overall mass balance and a mass balance of R-OH molecules leads to

$$\sum_i x_i^f + x_h^f = 1 \tag{43}$$

$$\sum_i i \cdot x_i^f = (x_a / x_h) \cdot x_h^f \quad . \tag{44}$$

The equilibrium constant, $K_i$, for the chemical reaction given by Equation (12) can be related to the mole fractions $x_1$, $x_{i-1}$, and $x_i$ as was done for $k_i$. If one then lets $K_2 = K_i$ for $i = 2$, and $K_3 = K_i$ for $i = 3,4,\ldots$ then the equilibrium constants can be shown to be related to each other by

$$k_i = K_2 \cdot (K_3)^{i-2} \quad . \tag{45}$$

Using Equation (37) then Equation (45) leads to an expression for the mole fraction of an i-mer as

$$x_i^f = K_2 \cdot (K_3)^{i-2} \cdot (x_1^f)^i \quad , \quad i \geq 2$$

$$= x_1^f \quad , \quad i = 1 \quad . \tag{46}$$

Equation (46) is used to put the infinite series in Equation (43) and (44) into closed form with the mathematical stipulation that $(K_3 \cdot x_1^f) < 1$. Then Equations (43) and (44) are combined to yield a cubic equation to be solved for $x_1^f$, the final monomer mole fraction*

$$a \cdot y^3 + b \cdot y^2 + c \cdot y + d = 0 \tag{47}$$

where

$$a = K_3 \cdot (K_3 - K_2)$$

$$b = - [(K_3^2 + K_2) \cdot x_a + 2 \cdot (K_3 - K_2)]$$

$$c = 1 + 2 \cdot K_3 \cdot x_a$$

$$d = - x_a$$

$$y = x_1^f \quad .$$

The solution of the physically significant root of Equation (47) is discussed in more detail in Appendix I. Similar mass and chemical balances for the initial unmixed state lead to a quadratic equation which can be solved for $x_1^i$, the initial monomer mole fraction (again the mathematical stipulation that $(K_3 x_1^i) < 1$ is present)

$$x_1^i = \frac{f - \mathrm{SQRT}(f^2 - 4 \cdot g)}{2 \cdot g} \tag{48}$$

* There is a misprint in references 17 and 18. The coefficient of the $y^2$ term in Equation (47) should be negative.

where

$$f = 1 + K_3$$

$$g = K_3 - K_2 \quad .$$

Only the negative root is physically significant. The mole fraction of the solvent, $x_h^f$, is found by solving either Equation (43) or (44) for this quantity. Equation (44) (the reason for this choice is given in Appendix I) leads to

$$x_h^f = \frac{1 - (1 + K_3)\cdot(x_1^f) + (K_3 - K_2)\cdot(x_1^f)^2}{1 - K_3\cdot(x_1^f)} \quad . \qquad (49)$$

All of the quantities in the expression for the excess Gibbs free energy, Equation (41), have now been specified.

Equation (42) for the excess enthalpy can be expressed in terms of known variables by using 1) the definition of the mole fractions $x_1^f$ and $x_i^i$ and 2) an expression for $h_i^o$ in terms of $H_i$ ($h_i^o = (i-2)H_3 + H_2$, for $i \geq 2$, and $h_1 = H_1 = 0$). The quantities $h_i^o$ and $H_i$ are enthalpy changes for the formation of an i-mer as given by Equations (36) and (12), respectively. For two equilibrium constants and two enthalpies of formation (one for dimerization, $K_2$ and $H_2$, and one for the reaction given by Equation (12) for $i > 1$, $K_3$ and $H_3$) the following form for the excess enthalpy is obtained*

* The equation was also deduced from the computer program given by Haskell[17] and agreed with the result derived in the present work.

$$H^E = A + B \tag{50}$$

where

$$A = x_a\left[\frac{1}{J} - \frac{x_h(1 - x_h^f)}{x_a x_h^f}\right](2 H_3 - H_2)$$

$$B = \left[\frac{x_1^i x_a}{J} - \frac{x_1^f x_h}{x_h^f}\right](H_2 - H_3)$$

$$J = \frac{n_a}{\sum_i n_i^i} = \frac{1}{\sum_i i \cdot x_i^i} \quad .$$

The quantity J is the average i-mer chain length in the pure alcohol. In deriving the expression given in Equation (50), the assumption has to be made that the difference between $n_1^i$ (the number of moles of monomer in the pure alcohol) and $n_1^f$ (the number of moles of monomer in the final mixture) is negligible. The quantities in Equation (50) are known or given by Equations (46), (47), and (48).

## Results and Discussion

Expressions have been derived for the excess Gibbs free energy and the excess enthalpy from two variations of the associated theory of solutions. A detailed method for the determination of the parameters is given in Appendix I. A brief description is given below.

The quantities, $G^E$ and $H^E$, can be calculated for the volume fraction model from Equations (24) and (50) respectively once the parameters K, $H^\circ$, $\beta$, and $\beta'$ have been specified. The $H^\circ$, -7500

cal./gm. mole and the K's at 50°C suggested by Renon and Prausnitz[44] are used for ethanol + n-heptane, 2-propanol + n-heptane, and ethanol + methylcyclohexane. Values of K at other temperatures are calculated from the van't Hoff relation with the assumption that $H^{O}$ is independent of temperature. The residual of the excess property is taken as being due to physical interaction. Therefore, the parameters $\beta$ and $\beta'$ are derived from the excess Gibbs free energy data and excess enthalpy data, respectively, by a least square procedure. The parameters used are given in Table 39, Appendix I. A comparison is made of the quantities $G_p^E$, $G_c^E$, and $G^E$ with the derived $G^E$ values in Table 40 and of the quantities $H_p^E$, $H_c^E$, and $H^E$ with the derived $H^E$ values in Table 41, Appendix I. The comparisons are made at 213.15, 243.15, 273.15, and 303.15 K for ethanol + n-heptane and ethanol + methylcyclohexane and at 183.15, 213.15, 243.15, 273.15, and 303.15 K for 2-propanol + n-heptane.

In an attempt to find an improved correlation of the excess property data, three variations of the volume fraction model were studied. These variations included 1) varying $H^{O}$ but keeping it temperature independent, 2) varying the equilibrium constant at 50°C, and 3) making $H^{O}$ temperature dependent

$$H^{O} = H^{O}(323.15) + A(T - 323.15) \quad .$$

The results of these variations are discussed in more detail in Appendix I. The first two variations gave worse overall correlations of the excess properties. The third variation resulted in a slightly

improved correlation, but did not warrant the addition of a new adjustable parameter.

The volume fractions are calculated on the assumption that the volume of mixing is negligible. The density data that are used are those of the API[47] for n-heptane from 120 to -60°C (10 degree intervals) and for methylcyclohexane from 100 to -130°C (10 degree intervals), those of Korber[28] for ethanol from 193 to 293 K (gave smoothed fit for interpolation purposes), and those of Costello and Bowden[7] from 80 to -60°C (below -60°C linear extrapolation was used graphically; they gave data at 20 degree intervals so linear interpolation was used).

The quantities $G^E$ and $H^E$ can be calculated for the mole fraction model from Equations (41) and (50) respectively once the parameters $K_2$, $K_3$, $H_2$, and $H_3$ have been specified. The parameters given by Haskell et al.[18] for the ethanol + n-heptane system at 288.15 K are used. Values of $K_2$, $K_3$, $H_2$, and $H_3$ at other temperatures are calculated using the van't Hoff relation. The parameters used for ethanol + n-heptane are given in Table 42, Appendix I. A comparison is made of the $G^E$ calculated from the mole fraction model to the derived $G^E$ in Table 43, Appendix I. A comparison is made of $H^E$ calculated from the mole fraction model to the derived $H^E$ in Table 44, Appendix I. The comparisons are made at 213.15, 243.15, 273.15, and 303.15 K for ethanol + n-heptane. It would have been interesting to test this model to the other two alcohol systems but time did not permit determination of the parameters.

The correlation of the excess property data with the two variations of the associated theory of solutions is discussed in Appendix I. The results of the theoretical analysis of the excess properties are illustrated in Figure 6 thru 9 for ethanol + n-heptane from 213.15 to 303.15 K. In these figures the solid curves $G^E$ and $H^E$ are the properties derived from excess heat capacities and are given in Appendix C.

An attempt was made to determine sets of parameters which satisfied the following criteria

1. The van't Hoff relation
2. The derived excess Gibbs free energy data
3. The derived excess enthalpy data.

The first criterion is met, since it is an imposed condition. How well the other criteria are satisfied may be judged from Figures 6 thru 9. At higher temperatures both models give a fairly good representation of the data. However, at lower temperatures when the physical interactions become more important the volume fraction model represents the data more satisfactorily. This suggests an important possible modification of the mole fraction model, namely, the inclusion of a physical interaction term. The alteration of the model to include physical interactions would require a decrease of the effect attributed to the breaking of hydrogen bonds or a strong temperature dependence for the physical interaction effect.

In a spectroscopic study made by Van Ness, et al.[61] evidence is found for the existence of an enthalpy other than that due to the breaking of hydrogen bonds. They deduced that this contribution

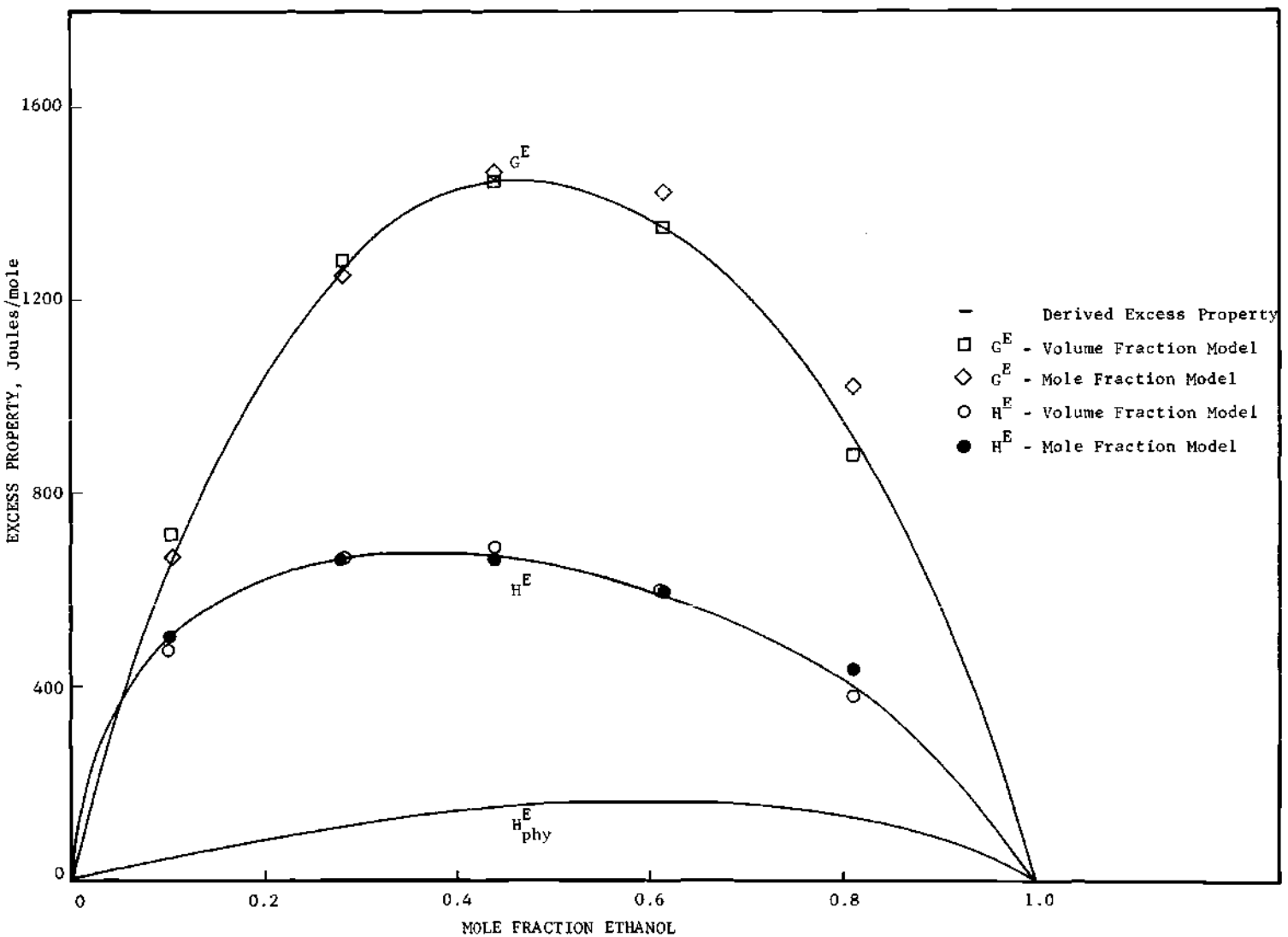


Figure 6. Excess Properties of Ethanol + n-Heptane at 303.15 K Compared with Theoretical Calculations.

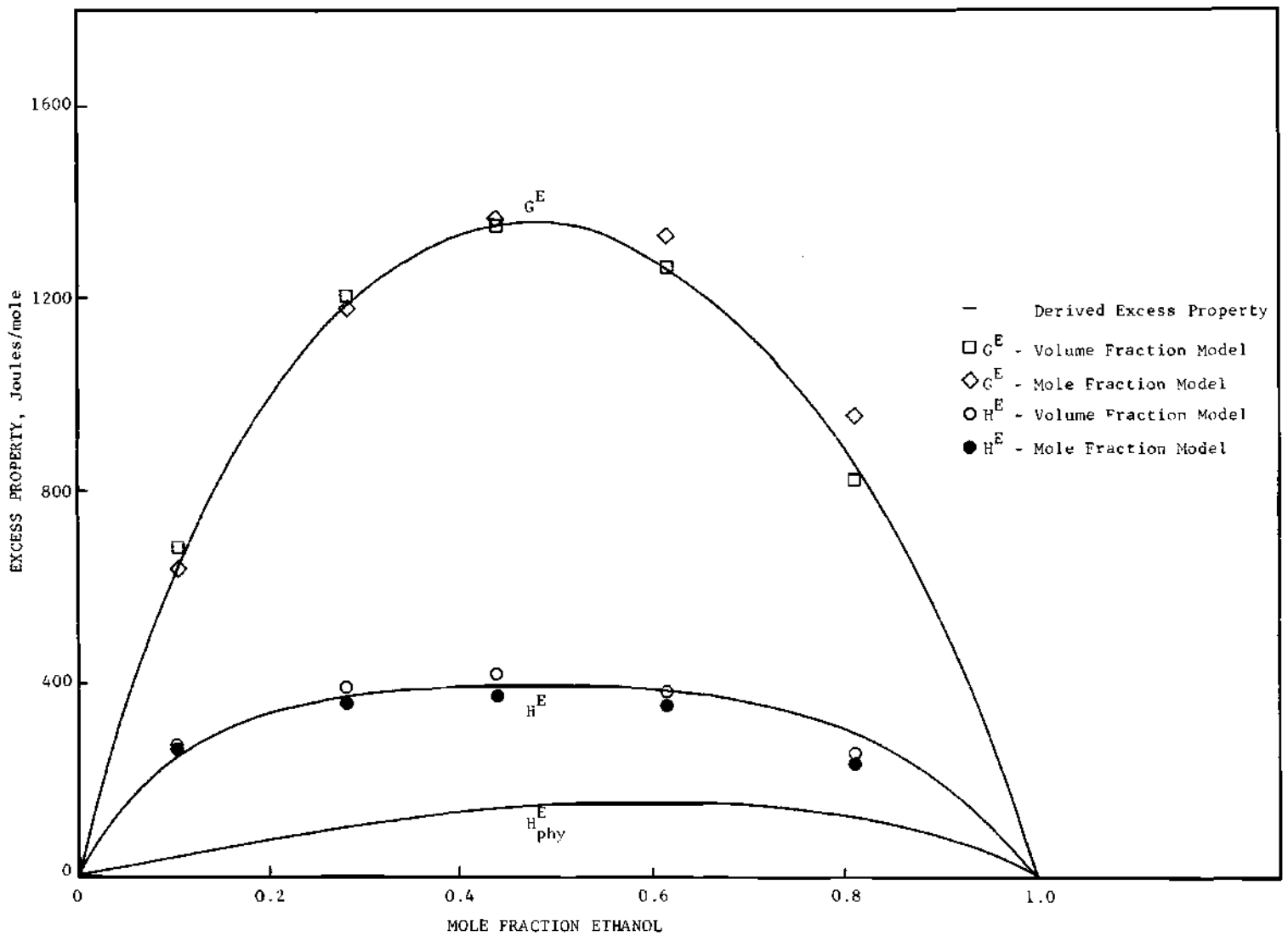


Figure 7. Excess Properties of Ethanol + n-Heptane at 273.15 K Compared with Theoretical Calculations.

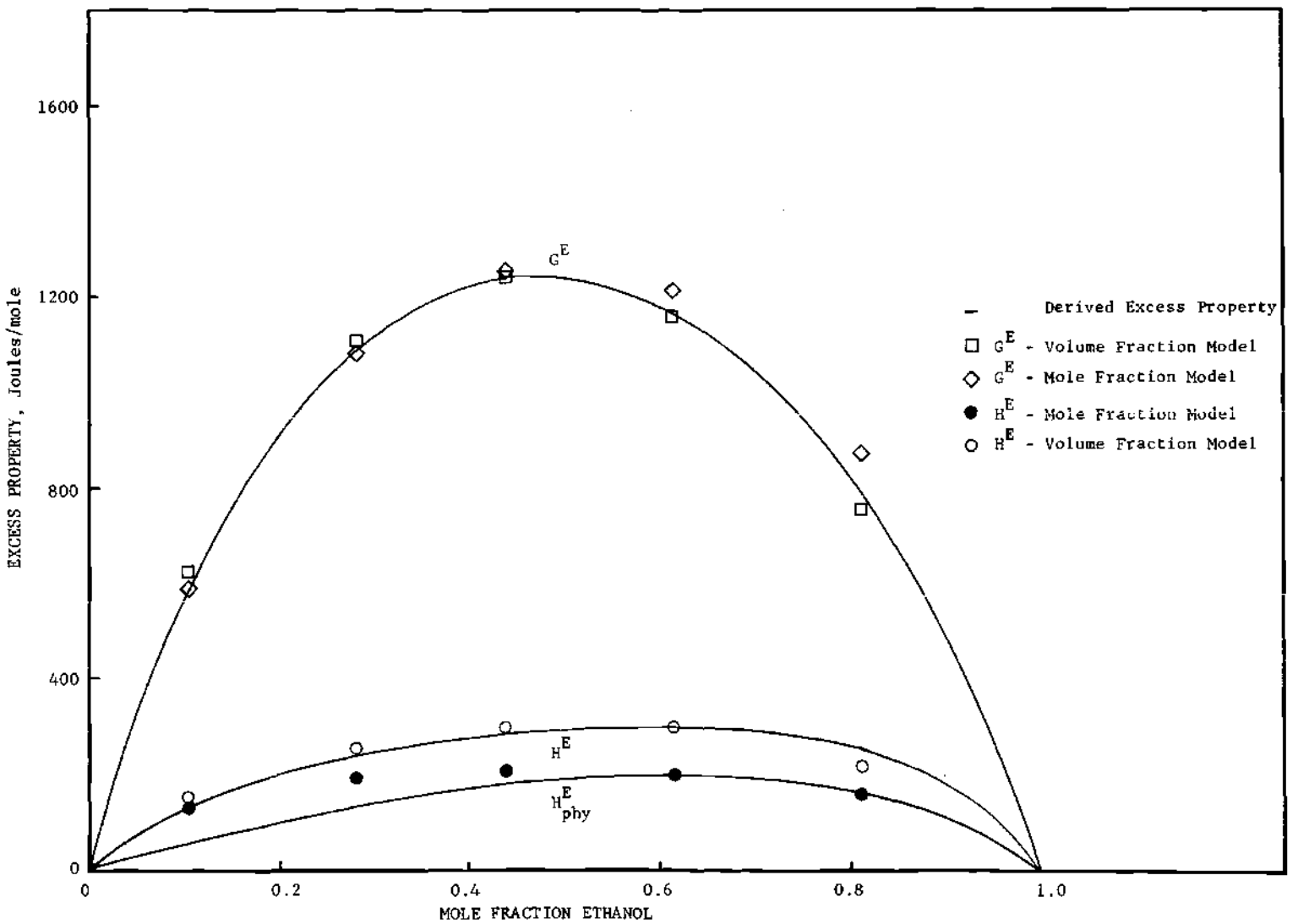


Figure 8. Excess Properties of Ethanol + n-Heptane at 243.15 K Compared with Theoretical Calculations.

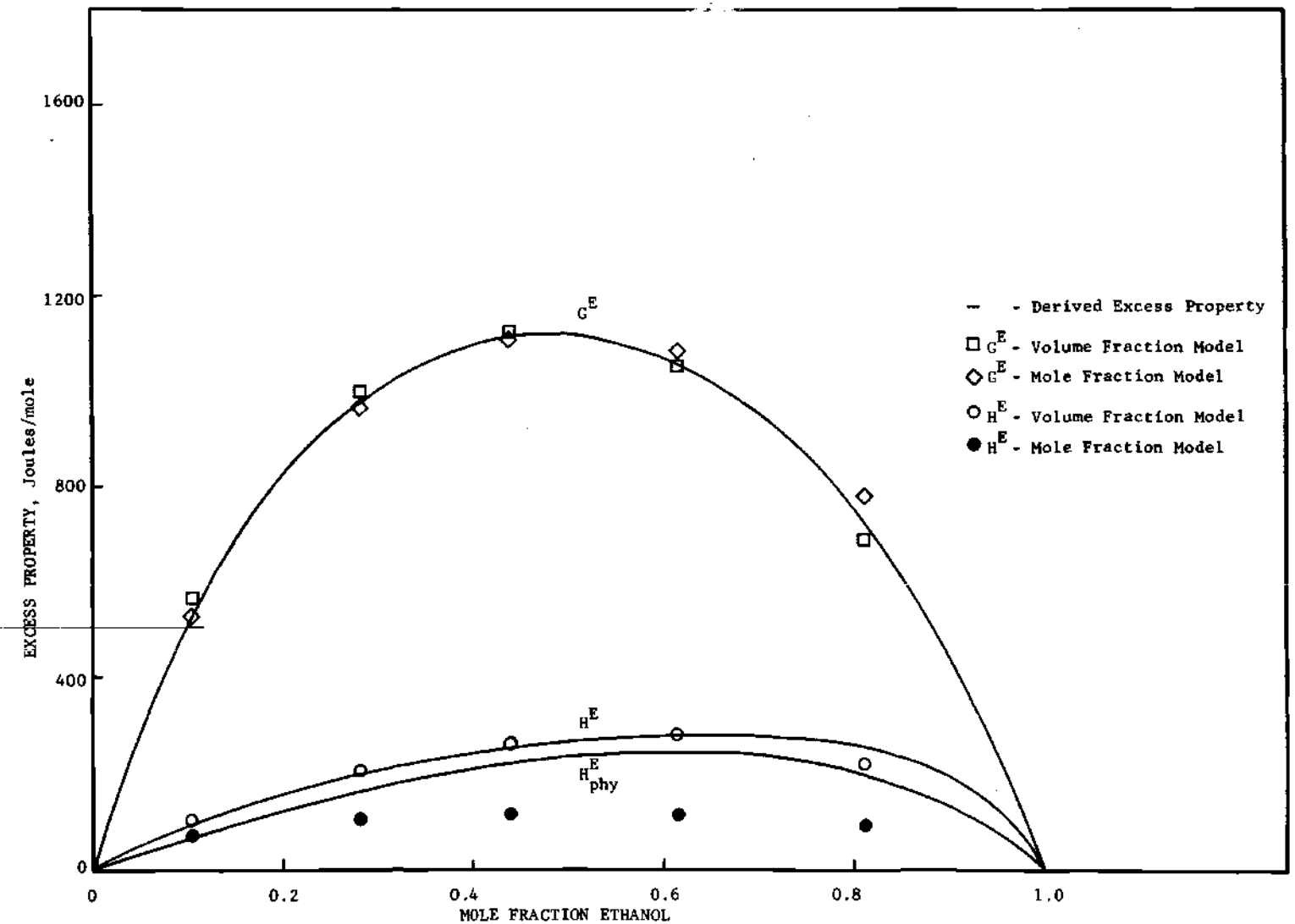


Figure 9. Excess Properties of Ethanol + n-Heptane at 213.15 K Compared with Theoretical Calculations.

increased with increasing temperature. In the present results this enthalpy contribution is attributed to van der Waal type interactions and increases with decreasing temperature. In a systematic calorimetric study made by Lunberg[32], the heats of mixing were determined for a large number of systems in which physical interactions are prominent. His results are that all of the heats of mixing of the systems increased with decreasing temperature.

Figures 6 thru 9 suggest the heat effect arising from the breaking of hydrogen bonds decreases with temperature and is negligible at lower temperatures. This is the conclusion drawn in the qualitative discussion in Chapter IV. Hwa[21] reached this same conclusion but attributed this decrease to the decrease of the enthalpy of formation of a hydrogen bond, $H^{o}$. In contrast the present author attributes this decrease to an increase in the equilibrium constant, which suggests that higher order i-mers are favored at lower temperatures. Indeed calculations show that the average i-mer chain length increases with decreasing temperature as shown for ethanol + n-heptane in Table 4.

Each model gives a consistent interpretation of the major interaction occurring at higher temperatures. The volume fraction model correlates the $G^{E}$ and $H^{E}$ data, within the bounds of the previously mentioned criteria and with fewer parameters. In fact a mole fraction model with one equilibrium constant does not predict the observed assymmetry of the excess enthalpy or excess entropy except with the addition of a second equilbrium constant or the introduction of a physical interaction term. Therefore for the sake of mathematical

simplicity without the loss of a reasonable interpretation of the experimental data, the volume fraction model is recommended.

Table 4. Average Chain Length for Ethanol + n-Heptane Solutions From the Volume Fraction Model.*

| | Temperature, K | | | |
|---|---|---|---|---|
| | 303.15 | 273.15 | 243.15 | 213.15 |
| $x_a$ | $N_{av}$ | $N_{av}$ | $N_{av}$ | $N_{av}$ |
| 0.1023 | 4.28 | 7.96 | 18.01 | 52.70 |
| 0.2805 | 7.11 | 13.61 | 31.29 | 92.31 |
| 0.4388 | 9.28 | 17.91 | 41.40 | 122.47 |
| 0.6140 | 11.71 | 22.74 | 52.73 | 156.26 |
| 0.8107 | 14.79 | 28.84 | 67.03 | 198.86 |
| 1.0000 | 18.47 | 36.21 | 83.96 | 249.38 |

* Average Chain Length = $\frac{1}{1-K \cdot \Phi_1}$ .

# CHAPTER VI

# CONCLUSIONS AND RECOMMENDATIONS

## Summary of Results

The work which has been completed can be summarized as follows:

1. The heat capacity of ethanol, 2-propanol, and n-heptane has been measured from 159 to 306 K, 185 to 304 K, and 182 to 302 K, respectively. The melting points of pure ethanol, 2-propanol, and n-heptane have been measured to be 158.991 K, 185.232 K, and 182.562 K. The purity of the components have been determined from the melting point experiments. The heat capacity of ethanol + n-heptane has been measured from 215 to 305 K at mole fractions of ethanol of 0.1023, 0.2805, 0.4388, 0.6140, and 0.8107. The heat capacity of 2-propanol + n-heptane has been measured from 187 to 305 K at mole fractions of 2-propanol of 0.0809, 0.2492, 0.4219, 0.5993, and 0.7984.

2. The heat capacity measurements have been used to calculate the excess heat capacity. From the excess heat capacity and from experimental data for $H^E$ and $G^E$ at 303.15 K taken from the literature, the properties $H^E$, $G^E$, $S^E$, and $\Delta G^M$ have been derived at five degree intervals from 183 to 318 K for ethanol + n-heptane and from 163 to 318 K for 2-propanol + n-heptane. The excess Gibbs free energy data for both systems are correlated empirically using the Redlich-Kister equation, a modified form of the Redlich-Kister equation, and the Wilson equation. The $G^E$ data are also correlated by the semi-empirical Wiehe-Bagley

equation. Each of these correlations are used to calculate the activity coefficients at 0.1 mole fraction intervals for ethanol + n-heptane at 303.15, 273.15, 143.15, and 213.15 K and for 2-propanol + n-heptane at 303.15, 273.15, 243.15, 213.15, and 183.15 K. Excess enthalpy data were extracted from the Wiehe-Bagley equation for the two systems at the same temperatures.

3. A volume fraction associated theory model, as developed by Renon and Prausnitz[44], was used to correlate the $G^E$ and $H^E$ data of ethanol + n-heptane and ethanol + methylcyclohexane at 213.15, 243.15, 273.15, and 303.15 K and of 2-propanol + n-heptane at 183.15, 213.15, 243.15, 273.15, and 303.15 K. The parameters used in this treatment include an enthalpy of formation of a hydrogen bond, $H^o$, the physical interaction parameters, $\beta$ and $\beta'$, and an equilibrium constant for the formation of an i+1-mer from an i-mer, K.

4. A mole fraction associated theory model, as developed by Haskell et al.[18], was used to correlate the $G^E$ and $H^E$ data of ethanol + n-heptane at 213.15, 243.15, 273.15, and 303.15 K. The parameters used in this treatment include $H_2$ and $H_3$, which are enthalpies of formation of a hydrogen bond in the dimerization and i-merization reactions respectively. Two equilibrium constants, $K_2$ and $K_3$, are for the same two reactions respectively.

## Conclusions

From the experimental measurements the following conclusions are made:

1) The calorimetric determinations of purity and melting point of ethanol, 2-propanol, and n-heptane indicate that the present measurements are consistent with other laboratories making precision measurements on the International Practical Temperature Scale.

2) The heat capacity data for the pure components, which are accurate to 0.2 per cent, agree with measurements made by other investigators. The excess heat capacity data of the binary mixtures are accurate to 0.15 to 0.07 Joule/gm. mole from pure n-heptane to pure alcohol respectively. The excess heat capacity for ethanol + n-heptane agree with other measurements near room temperature. The excess heat capacity for 2-propanol + n-heptane have not been measured before.

From the derived excess thermodynamic properties of $H^E$, $G^E$, and $S^E$ the following conclusions are made:

1) The excess thermodynamic property data for ethanol + n-heptane and 2-propanol + n-heptane are the best available below 303.15 K. The derived excess enthalpy has an uncertainty of 4 to 12 Joules/gm. mole at 303.15 K increasing to 17 to 26 Joules/gm. mole at 183.15 K. The derived excess Gibbs free energy has an uncertainty of 2 to 7 Joules/gm. mole at 303.15 K increasing to 6 to 13 Joules/gm. mole at 183.15 K. The derived excess entropy has an uncertainty of 0.02 to 0.06 Joule/gm. mole-K at 303.15 increasing to 0.08 to 0.16 Joule/gm. mole-K at 183.15 K.

2) The temperature dependence of the excess enthalpy and excess entropy suggests that the number of hydrogen bonds broken decreases with decreasing temperature. At lower temperatures the excess enthalpy

and excess entropy are almost independent of temperature. This is interpreted as meaning that the contribution due to the breaking of the hydrogen bonds decreases at such a rate as to cancel the increase of the contribution due to van der Waals interactions.

3) The excess Gibbs free energy data can be correlated empirically within their uncertainty by the Redlich-Kister equation, a modified form of the Redlich-Kister equation, and the Wilson equation. These data can also be correlated with the semi-empirical Wiehe-Bagley equation. The excess enthalpy predicted from the Wiehe-Bagley equation represents the qualitative behavior of the alcohol-hydrocarbon systems.

From the theoretical analysis of the derived excess thermodynamic properties the following conclusions are made:

1) From the derived excess Gibbs free energy and excess enthalpy data the parameters of two variations of the associated theory of solutions (the volume fraction and mole fraction models) were determined. The equilibrium constants were constrained to obey the van't Hoff relation. The physical interaction parameter was determined by a least square procedure.

2) The volume fraction model is only able to correlate both the excess Gibbs free energy and excess enthalpy data as well as it does by making the excess enthalpy due to physical interactions be temperature dependent. The resulting volume fraction model gives a better correlation of the $G^E$ and $H^E$ data than does the mole fraction model.

3) The mole fraction model, which only considers chemical interactions due to the breaking of hydrogen bonds, correlates the data less

satisfactorily at lower temperatures where this contribution to the excess enthalpy is small.

4) Both models predict that the contribution to the excess enthalpy due to the breaking of the hydrogen bonds decreases with decreasing temperature. The decrease of the chemical effect is due to the decrease of the number of hydrogen bonds broken, not the radical decrease of the enthalpy of formation of a hydrogen bond. The present results indicate that a second type interaction is present. This interaction which is attributed to van der Waals type, increases slightly as the temperature decreases.

## Recommendations for Future Work

1) The volume fraction model should be pursued further since it gives reasonable conclusions yet keeps its mathematical simplicity by introducing as few adjustable parameters as possible.

2) The mole fraction model should be extended to other alcohol-hydrocarbon systems to see if the same conclusions are reached for systems in which the molar volume ratio is different.

3) The mole fraction model be modified to incorporate a physical interaction term. An investigation of the one equilibrium constant mole fraction model with this same modification seems reasonable.

# APPENDICES

# APPENDIX A

## NUMERICAL CONSTANTS AND CONVERSIONS USED IN CALCULATIONS

### Temperature Scale

All temperature measurements were made with a platinum resistance thermometer. The thermometer has been calibrated on the International Practical Temperature Scale of 1948 by the U.S. National Bureau of Standards. All interconversions of temperature to the Kelvin scale were made using the relation

$$T(K) = t(^{o}C) + 273.15$$

and are referred to as IPKS-54. Conversion from the IPTS of 1948 to the IPTS of 1968 has been made by fitting the difference between the scales[2] to a tenth degree polynominal of the form

$$t_{68} - t_{48} = \sum_{i=0}^{10} P_i \, t_{68}^{i} \, .$$

The coefficients of the polynomial are given in Table 5. The fit was made from a temperature of -180 to 100°C. The fit agreed with the differences given by the U.S. National Bureau of Standards with an average deviation of 0.2 millidegrees and a maximum deviation of 0.5 millidegrees.

Table 5. Coefficients of the Temperature Difference Between the International Practical Temperature Scale of 1968 (IPTS-68) and the International Practical Temperature Scale of 1948 (IPTS-48)

| Coefficient | | Coefficient | |
|---|---|---|---|
| $P_0$ | 3.96206547 (-04)* | $P_6$ | 4.06683898 (-14) |
| $P_1$ | -4.91955928 (-04) | $P_7$ | 5.11588793 (-16) |
| $P_2$ | 5.18664917 (-06) | $P_8$ | 7.97726901 (-20) |
| $P_3$ | 4.61114615 (-08) | $P_9$ | -2.58971781 (-20) |
| $P_4$ | -7.33468174 (-10) | $P_{10}$ | -9.27499543 (-23) |
| $P_5$ | -3.33127229 (-12) | | |

* Numbers in parenthesis indicate multiplication by 10 raised to this power.

## Molecular Weights

The molecular weights of the constituents used in this work were calculated on the basis of the 1961 Table of International Atomic Weights.[66] The atomic weights of carbon, hydrogen, and oxygen are

| | |
|---|---|
| Carbon | 12.01115 ± 0.00005 |
| Hydrogen | 1.00797 ± 0.00001 |
| Oxygen | 15.9994 ± 0.0001 . |

The molecular weights calculated for ethanol, 2-propanol, n-heptane, and methylcyclohexane are

| | |
|---|---|
| Ethanol | 46.06952 ± 0.00026 |
| 2-Propanol | 60.09661 ± 0.00033 |
| n-Heptane | 100.20557 ± 0.00051 |
| Methylcyclohexane | 98.18963 ± 0.00049 |

## Energy Conversion

Energy measurements were made on the absolute scale. Interconversion of energy from the defined calorie to the absolute joule were made using the relation

4.184 Absolute Joules = 1 Defined Calorie .

# APPENDIX B

## HEAT CAPACITY DATA*

Table 6. Heat Capacity of n-Heptane

(Sample weight in vacuo = 104.541 gms.)

| Initial Temp. K | Mean Temp. K | Heat Capacity Joules/gm. mole-K |
|---|---|---|
| | Series 2 | |
| 184.220 | 187.228 | 201.96 |
| 190.236 | 193.416 | 201.30 |
| 196.597 | 199.609 | 201.11 |
| 202.622 | 205.420 | 201.27 |
| 208.217 | 211.049 | 201.64 |
| | Series 3 | |
| 198.198 | 200.938 | 200.72 |
| 203.677 | 206.815 | 201.06 |
| 209.953 | 213.230 | 201.67 |
| 216.506 | 219.722 | 202.48 |
| 222.938 | 225.813 | 203.45 |
| 228.688 | 231.511 | 204.40 |
| 234.334 | 237.176 | 205.63 |
| 240.018 | 243.004 | 207.08 |
| 245.991 | 248.710 | 208.50 |
| 251.428 | 254.484 | 210.12 |
| 257.541 | 260.725 | 211.90 |
| 263.909 | 266.882 | 213.68 |
| 269.855 | 272.671 | 215.73 |
| 275.487 | 277.628 | 217.10 |

(Continued)

*All temperatures are on IPTS-68. Series is defined as a range of temperature measured consecutively.

Table 6. Heat Capacity of n-Heptane (Continued).

| Initial Temp. K | Mean Temp. K | Heat Capacity Joules/gm. mole-K |
|---|---|---|
| | Series 1 | |
| 273.748 | 275.669 | 216.61 |
| 277.589 | 279.661 | 217.93 |
| 281.733 | 283.716 | 219.47 |
| 285.699 | 287.673 | 220.80 |
| 289.646 | 291.395 | 222.27 |
| 293.145 | 295.399 | 223.82 |
| 297.654 | 299.365 | 225.30 |
| 301.076 | 302.739 | 226.66 |
| | Series 4 | |
| 273.518 | 275.381 | 216.30 |
| 277.244 | 279.743 | 217.91 |
| 282.241 | 284.723 | 219.48 |
| 296.732 | 296.732 | 224.68 |
| 301.785 | 304.562 | 226.88 |

Table 7. Heat Capacity of 2-Propanol

(Sample weight in vacuo = 119.844 gms.)

| Initial Temp. K | Mean Temp. K | Heat Capacity Joules/gm. mole-K |
|---|---|---|
| | Series 1 | |
| 188.438 | 191.571 | 109.89 |
| 194.704 | 197.374 | 110.96 |
| 200.043 | 202.397 | 111.88 |
| | Series 3 | |
| 195.857 | 198.496 | 111.10 |
| 201.136 | 204.199 | 112.24 |
| 207.262 | 209.854 | 113.41 |
| 212.446 | 215.191 | 114.71 |
| 217.936 | 220.503 | 116.09 |
| 223.070 | 225.567 | 117.48 |
| 228.064 | 230.560 | 118.96 |
| 231.859 | 234.335 | 120.22 |
| 236.810 | 239.365 | 121.95 |
| 241.920 | 244.488 | 123.91 |
| 247.056 | 249.588 | 125.93 |
| 252.122 | 254.674 | 128.13 |
| 257.226 | 259.785 | 130.53 |
| 262.344 | 264.969 | 133.15 |
| 267.595 | 270.384 | 136.21 |
| 273.173 | 275.591 | 139.18 |
| | Series 2 | |
| 273.260 | 275.355 | 138.79 |
| 277.450 | 279.544 | 141.53 |
| 281.639 | 283.857 | 144.41 |
| 286.076 | 288.597 | 147.62 |
| 291.118 | 293.719 | 151.30 |
| 296.320 | 298.948 | 155.48 |
| 301.577 | 303.819 | 159.31 |

Table 8. Heat Capacity of Ethanol

(Sample weight in vacuo = 121.608 gms.)

| Initial Temp. K | Mean Temp. K | Heat Capacity Joules/gm. mole-K |
|---|---|---|
| | Series 1 | |
| 160.357 | 162.361 | 87.60 |
| | Series 2 | |
| 159.400 | 161.706 | 87.60 |
| 164.012 | 166.446 | 87.78 |
| 168.880 | 171.324 | 87.95 |
| 173.768 | 176.176 | 88.13 |
| 178.585 | 180.998 | 88.38 |
| 183.412 | 185.818 | 88.67 |
| 188.224 | 190.668 | 89.06 |
| 193.114 | 195.486 | 89.48 |
| 197.858 | 200.226 | 89.87 |
| | Series 3 | |
| 197.640 | 200.003 | 89.91 |
| 202.366 | 204.757 | 90.39 |
| 207.148 | 209.560 | 90.91 |
| 211.972 | 214.409 | 91.53 |
| 216.846 | 219.264 | 92.16 |
| 221.683 | 224.142 | 92.90 |
| 226.602 | 229.150 | 93.66 |
| 231.697 | 234.105 | 94.48 |
| 236.512 | 238.948 | 95.34 |
| 238.655 | 241.080 | 95.79 |
| 243.504 | 245.973 | 96.80 |
| 248.442 | 250.943 | 97.90 |
| 253.444 | 255.962 | 98.97 |
| 258.480 | 261.005 | 100.21 |
| 263.530 | 266.101 | 101.50 |
| 268.673 | 271.205 | 102.89 |
| 273.736 | 276.220 | 104.31 |

(Continued)

Table 8. Heat Capacity of Ethanol (Continued)

| Initial Temp. K | Mean Temp. K | Heat Capacity Joules/gm. mole-K |
|---|---|---|
| | Series 4 | |
| 273.583 | 276.056 | 104.44 |
| 278.529 | 280.985 | 106.03 |
| 283.442 | 285.925 | 107.67 |
| 288.408 | 290.889 | 109.38 |
| 293.370 | 295.858 | 111.27 |
| 298.347 | 300.845 | 113.22 |
| 303.343 | 305.888 | 115.36 |

Table 9. Heat Capacity of 2-Propanol + n-Heptane

$x_a = 0.0809$

(Sample weight in vacuo = 103.210 gms.)

| Initial Temp. K | Mean Temp. K | Heat Capacity Joules/gm. mole-K | Excess Heat Capacity Joules/gm. mole-K |
|---|---|---|---|
| | | Series 3 | |
| 187.936 | 190.264 | 194.62 | 0.49 |
| 192.592 | 195.021 | 194.51 | 0.70 |
| 197.450 | 199.923 | 194.58 | 0.83 |
| | | Series 4 | |
| 195.272 | 197.712 | 194.45 | 0.70 |
| 200.152 | 202.656 | 194.68 | 0.88 |
| 205.161 | 207.690 | 195.06 | 0.97 |
| 210.219 | 212.772 | 195.75 | 1.18 |
| 215.326 | 217.863 | 196.59 | 1.38 |
| 220.400 | 222.913 | 197.65 | 1.66 |
| 225.427 | 227.947 | 198.71 | 1.81 |
| 230.467 | 232.704 | 200.06 | 2.19 |
| 234.941 | 237.424 | 201.40 | 2.48 |
| 239.907 | 242.321 | 203.07 | 2.97 |
| | | Series 2 | |
| 242.162 | 244.503 | 203.78 | 3.12 |
| 246.845 | 249.298 | 205.51 | 3.58 |
| 251.752 | 254.246 | 207.62 | 4.29 |
| 256.741 | 259.263 | 209.60 | 4.76 |
| 261.786 | 264.318 | 211.97 | 5.54 |
| 266.850 | 269.398 | 214.34 | 6.23 |
| 271.946 | 274.526 | 217.02 | 7.12 |
| | | Series 1 | |
| 273.197 | 275.477 | 217.36 | 7.12 |
| *277.758 | 280.248 | 219.73 | 7.75 |
| 282.739 | 285.235 | 222.56 | 8.70 |
| 287.731 | 290.249 | 225.34 | 9.52 |

*Data used in sample calculation.

(Continued)

Table 9. Heat Capacity of 2-Propanol + n-Heptane (Continued)

| Initial Temp. K | Mean Temp. K | Heat Capacity Joules/gm. mole-K | Excess Heat Capacity Joules/gm. mole-K |
|---|---|---|---|
| 292.766 | 295.312 | 228.17 | 10.33 |
| 297.858 | 300.407 | 231.12 | 11.18 |
| 302.956 | 305.479 | 234.02 | 11.99 |

(Continued)

Table 9. Heat Capacity of 2-Propanol + n-Heptane (Continued)

$x_a = 0.2492$

(Sample weight in vacuo = 105.164 gms.)

| Initial Temp. K | Mean Temp. K | Heat Capacity Joules/gm. mole-K | Excess Heat Capacity Joules/gm. mole-K |
|---|---|---|---|
| | | Series 4 | |
| 187.975 | 190.413 | 179.11 | 0.45 |
| 192.851 | 195.330 | 179.43 | 0.87 |
| 197.808 | 200.281 | 179.78 | 1.10 |
| | | Series 5 | |
| 195.518 | 197.997 | 179.53 | 0.94 |
| 200.476 | 202.937 | 180.12 | 1.29 |
| 205.398 | 207.833 | 180.86 | 1.61 |
| 210.268 | 212.700 | 181.74 | 1.91 |
| 215.133 | 217.570 | 182.77 | 2.23 |
| 220.006 | 222.427 | 183.92 | 2.54 |
| 224.849 | 227.254 | 185.18 | 2.83 |
| | | Series 3 | |
| 227.990 | 230.306 | 186.13 | 3.12 |
| 232.623 | 235.080 | 187.79 | 3.67 |
| 237.536 | 240.050 | 189.53 | 4.15 |
| 242.564 | 245.154 | 191.51 | 4.73 |
| 247.744 | 250.301 | 193.73 | 5.43 |
| | | Series 2 | |
| 252.012 | 254.367 | 195.45 | 5.88 |
| 256.722 | 259.152 | 197.61 | 6.46 |
| 261.583 | 264.059 | 200.07 | 7.21 |
| 266.534 | 269.100 | 202.85 | 8.14 |
| 271.665 | 274.285 | 205.84 | 9.11 |

(Continued)

Table 9. Heat Capacity of 2-Propanol + n-Heptane (Continued)

| Initial Temp. K | Mean Temp. K | Heat Capacity Joules/gm. mole-K | Excess Heat Capacity Joules/gm. mole-K |
|---|---|---|---|
| | | Series 1 | |
| 273.324 | 275.546 | 206.37 | 9.13 |
| 277.768 | 280.239 | 209.20 | 10.03 |
| 282.710 | 285.192 | 212.31 | 11.02 |
| 287.673 | 290.167 | 215.63 | 12.12 |
| 292.662 | 295.108 | 219.09 | 13.30 |
| 297.555 | 299.932 | 222.58 | 14.48 |
| 302.309 | 304.674 | 225.94 | 15.53 |

(Continued)

Table 9. Heat Capacity of 2-Propanol + n-Heptane (Continued)

$x_a = 0.4219$

(Sample weight in vacuo = 105.970 gms.)

| Initial Temp. K | Mean Temp. K | Heat Capacity Joules/gm. mole-K | Excess Heat Capacity Joules/gm. mole-K |
|---|---|---|---|
| | | Series 2 | |
| 188.448 | 190.820 | 162.74 | -0.07 |
| 193.193 | 195.605 | 163.23 | 0.31 |
| 198.017 | 200.528 | 163.89 | 0.65 |
| | | Series 3 | |
| 195.534 | 197.863 | 163.54 | 0.49 |
| 200.192 | 202.682 | 164.29 | 0.86 |
| 205.171 | 207.588 | 165.23 | 1.25 |
| 210.004 | 212.381 | 166.27 | 1.61 |
| 214.758 | 217.254 | 167.51 | 2.03 |
| 219.750 | 222.244 | 168.93 | 2.48 |
| 224.739 | 227.119 | 170.39 | 2.89 |
| 229.260 | 231.724 | 171.95 | 3.34 |
| 234.189 | 236.599 | 174.00 | 4.11 |
| 239.009 | 241.430 | 176.02 | 4.77 |
| 243.850 | 246.333 | 178.12 | 5.38 |
| 248.065 | 250.577 | 180.01 | 5.90 |
| 253.089 | 255.633 | 182.67 | 6.81 |
| 258.176 | 260.644 | 185.39 | 7.69 |
| 263.112 | 265.570 | 188.05 | 8.43 |
| 268.029 | 270.490 | 191.27 | 9.61 |
| 272.951 | 275.312 | 194.34 | 10.58 |
| | | Series 1 | |
| 273.297 | 275.299 | 194.14 | 10.39 |
| 277.300 | 279.461 | 196.88 | 11.23 |
| 281.622 | 284.028 | 200.13 | 12.30 |
| 286.435 | 288.953 | 203.60 | 13.32 |
| 291.472 | 294.000 | 207.36 | 14.44 |
| 296.528 | 298.956 | 211.08 | 15.47 |
| 301.384 | 303.833 | 214.91 | 16.55 |

(Continued)

Table 9. Heat Capacity of 2-Propanol + n-Heptane (Continued)

$x_a = 0.5993$

(Sample weight in vacuo = 111.453 gms.)

| Initial Temp. K | Mean Temp. K | Heat Capacity Joules/gm. mole-K | Excess Heat Capacity Joules/gm. mole-K |
|---|---|---|---|
| | | Series 3 | |
| 188.374 | 190.696 | 145.66 | -0.87 |
| 193.018 | 195.518 | 146.38 | -0.48 |
| 198.019 | 200.486 | 147.18 | -0.18 |
| | | Series 4 | |
| 195.652 | 198.096 | 146.81 | -0.30 |
| 200.540 | 203.037 | 147.74 | 0.06 |
| 205.535 | 208.097 | 148.78 | 0.38 |
| 210.659 | 213.257 | 150.02 | 0.73 |
| 215.854 | 218.486 | 151.42 | 1.10 |
| 221.119 | 223.803 | 153.01 | 1.52 |
| 226.488 | 229.136 | 154.84 | 2.03 |
| 231.783 | 234.420 | 156.81 | 2.57 |
| 236.266 | 238.861 | 158.70 | 3.14 |
| 241.457 | 244.014 | 161.00 | 3.80 |
| 246.571 | 249.062 | 163.35 | 4.43 |
| 251.552 | 253.998 | 165.94 | 5.21 |
| 256.443 | 258.394 | 168.23 | 5.78 |
| | | Series 2 | |
| 257.634 | 259.944 | 169.16 | 6.08 |
| 262.252 | 264.769 | 172.08 | 6.97 |
| 267.286 | 269.825 | 175.32 | 7.94 |
| 272.364 | 274.866 | 178.81 | 9.03 |
| | | Series 1 | |
| 273.192 | 275.300 | 178.93 | 8.93 |
| 277.409 | 279.834 | 182.12 | 9.83 |
| 282.258 | 284.687 | 185.82 | 10.94 |
| 287.116 | 289.601 | 189.58 | 11.94 |
| 292.086 | 294.580 | 194.55 | 12.98 |
| 297.074 | 299.566 | 197.57 | 13.91 |
| 302.059 | 304.574 | 201.96 | 15.07 |

(Continued)

Table 9. Heat Capacity of 2-Propanol + n-Heptane (Continued)

$x_a = 0.7984$

(Sample weight in vacuo = 113.777 gms.)

| Initial Temp. K | Mean Temp. K | Heat Capacity Joules/gm. mole-K | Excess Heat Capacity Joules/gm. mole-K |
|---|---|---|---|
| | | Series 2 | |
| 188.460 | 190.772 | 127.10 | -1.17 |
| 193.084 | 195.467 | 127.87 | -0.96 |
| 197.850 | 200.263 | 128.83 | -0.68 |
| | | Series 3 | |
| 195.400 | 197.851 | 128.41 | -0.75 |
| 200.302 | 202.738 | 129.41 | -0.49 |
| 205.175 | 207.600 | 130.47 | -0.28 |
| 210.025 | 212.455 | 131.54 | -0.16 |
| 214.885 | 217.302 | 132.86 | 0.10 |
| 219.720 | 222.126 | 134.25 | 0.34 |
| 224.532 | 226.978 | 135.79 | 0.60 |
| 229.424 | 231.927 | 137.49 | 0.90 |
| 234.431 | 236.928 | 139.34 | 1.21 |
| 239.424 | 241.827 | 141.42 | 1.65 |
| | | Series 1 | |
| 241.701 | 244.068 | 142.15 | 1.58 |
| 246.435 | 248.876 | 144.50 | 2.15 |
| 251.318 | 253.754 | 146.96 | 2.66 |
| 256.190 | 258.672 | 149.50 | 3.11 |
| 261.154 | 263.693 | 152.39 | 3.71 |
| 266.231 | 268.782 | 155.49 | 4.34 |
| 271.333 | 273.973 | 158.95 | 5.10 |
| | | Series 4 | |
| 273.203 | 275.135 | 159.59 | 5.11 |
| 277.067 | 279.508 | 162.69 | 5.77 |
| 281.949 | 284.394 | 166.25 | 6.44 |
| 286.838 | 289.280 | 170.05 | 7.19 |
| 291.721 | 294.178 | 174.09 | 8.00 |
| 296.635 | 299.140 | 178.29 | 8.75 |
| 301.645 | 304.180 | 182.81 | 9.57 |

Table 10. Heat Capacity of Ethanol + n-Heptane

$x_a = 0.1023$

(Sample weight in vacuo = 105.337 gms.)

| Initial Temp. K | Mean Temp. K | Heat Capacity Joules/gm. mole-K | Excess Heat Capacity Joules/gm. mole-K |
|---|---|---|---|
| | | Series 2 | |
| 202.786 | 205.180 | 190.29 | 0.52 |
| 207.574 | 210.001 | 190.72 | 0.63 |
| 212.427 | 214.922 | 191.46 | 0.87 |
| 217.417 | 219.911 | 192.25 | 1.02 |
| 222.405 | 225.222 | 193.33 | 1.26 |
| 228.039 | 230.754 | 194.61 | 1.54 |
| | | Series 1 | |
| 233.344 | 235.806 | 196.04 | 1.95 |
| 238.269 | 240.736 | 197.45 | 2.28 |
| 243.202 | 245.692 | 198.99 | 2.64 |
| 248.182 | 250.669 | 200.66 | 3.05 |
| 253.156 | 255.665 | 202.54 | 3.59 |
| 258.174 | 260.679 | 204.64 | 4.25 |
| 263.185 | 265.694 | 206.72 | 4.84 |
| 268.203 | 270.701 | 209.19 | 5.73 |
| 273.199 | 275.698 | 211.40 | 6.31 |
| | | Series 3 | |
| 273.251 | 275.738 | 211.30 | 6.20 |
| 278.224 | 280.727 | 213.76 | 6.95 |
| 283.229 | 285.755 | 216.37 | 7.80 |
| 288.281 | 290.807 | 219.18 | 8.77 |
| 293.333 | 295.872 | 221.95 | 9.66 |
| 298.411 | 300.950 | 224.94 | 10.73 |
| 303.490 | 306.018 | 227.92 | 11.78 |

(Continued)

Table 10. Heat Capacity of Ethanol + n-Heptane (Continued)

$x_a = 0.2805$

(Sample weight in vacuo = 106.728 gms.)

| Initial Temp. K | Mean Temp. K | Heat Capacity Joules/gm. mole-K | Excess Heat Capacity Joules/gm. mole-K |
|---|---|---|---|
| | | Series 3 | |
| 218.856 | 221.353 | 173.03 | 1.23 |
| 223.850 | 226.334 | 173.97 | 1.37 |
| 228.817 | 231.291 | 175.12 | 1.63 |
| 233.764 | 236.210 | 176.51 | 2.04 |
| | | Series 2 | |
| 238.024 | 240.532 | 177.76 | 2.37 |
| 243.040 | 245.551 | 179.29 | 2.75 |
| 248.062 | 250.565 | 181.08 | 3.30 |
| 253.068 | 255.569 | 182.99 | 3.91 |
| 258.070 | 260.568 | 185.10 | 4.64 |
| 263.067 | 265.550 | 187.31 | 5.40 |
| 268.034 | 270.519 | 189.67 | 6.25 |
| 273.005 | 275.468 | 192.08 | 7.07 |
| | | Series 1 | |
| 274.148 | 276.382 | 192.36 | 7.05 |
| 278.615 | 281.082 | 194.91 | 8.02 |
| 283.550 | 286.018 | 197.65 | 9.03 |
| 288.486 | 290.959 | 200.60 | 10.19 |
| 293.433 | 295.893 | 203.60 | 11.36 |
| 298.354 | 300.808 | 206.75 | 12.63 |
| 303.262 | 305.722 | 210.09 | 14.05 |

(Continued)

Table 10. Heat Capacity of Ethanol + n-Heptane (Continued)

$x_a = 0.4388$

(Sample weight in vacuo = 106.415 gms.)

| Initial Temp. K | Mean Temp. K | Heat Capacity Joules/gm. mole-K | Excess Heat Capacity Joules/gm. mole-K |
|---|---|---|---|
| | | Series 3 | |
| 216.344 | 218.746 | 154.84 | 0.87 |
| 221.148 | 223.589 | 155.76 | 1.08 |
| 226.031 | 228.503 | 156.72 | 1.23 |
| 230.117 | 232.587 | 157.73 | 1.49 |
| 235.056 | 237.569 | 159.10 | 1.88 |
| 240.082 | 242.584 | 160.64 | 2.35 |
| 245.086 | 247.574 | 162.11 | 2.68 |
| | | Series 2 | |
| 248.127 | 250.600 | 163.14 | 2.97 |
| 253.073 | 255.625 | 164.95 | 3.51 |
| 258.177 | 260.689 | 166.91 | 4.10 |
| 263.115 | 265.627 | 169.10 | 4.90 |
| 268.139 | 270.641 | 171.43 | 5.72 |
| 273.144 | 275.636 | 173.77 | 6.48 |
| | | Series 1 | |
| 273.200 | 275.681 | 173.68 | 6.38 |
| 278.163 | 280.673 | 176.41 | 7.47 |
| 283.184 | 285.692 | 179.02 | 8.34 |
| 288.200 | 290.717 | 181.96 | 9.47 |
| 293.234 | 295.756 | 185.04 | 10.67 |
| 298.272 | 300.786 | 188.23 | 11.92 |
| 303.299 | 305.822 | 191.74 | 13.43 |

(Continued)

Table 10. Heat Capacity of Ethanol + n-Heptane (Continued)

$x_a = 0.6140$

(Sample weight in vacuo = 109.364 gms.)

| Initial Temp. K | Mean Temp. K | Heat Capacity Joules/gm. mole-K | Excess Heat Capacity Joules/gm. mole-K |
|---|---|---|---|
| | | Series 2 | |
| 211.670 | 214.056 | 134.36 | 0.32 |
| 216.441 | 218.856 | 135.08 | 0.42 |
| 221.271 | 223.781 | 135.89 | 0.50 |
| 226.290 | 228.781 | 136.88 | 0.67 |
| 231.271 | 233.750 | 138.06 | 0.96 |
| 236.228 | 238.799 | 139.31 | 1.23 |
| 238.864 | 241.320 | 140.06 | 1.46 |
| 243.777 | 246.204 | 141.40 | 1.74 |
| 248.630 | 251.075 | 143.07 | 2.28 |
| 253.520 | 255.916 | 144.55 | 2.56 |
| 258.313 | 260.738 | 146.24 | 2.99 |
| 263.150 | 265.581 | 148.06 | 3.47 |
| 268.012 | 270.462 | 150.15 | 4.13 |
| 272.911 | 275.374 | 152.31 | 4.78 |
| | | Series 1 | |
| 273.215 | 275.644 | 152.33 | 4.72 |
| 278.072 | 280.527 | 154.68 | 5.48 |
| 282.981 | 285.431 | 157.20 | 6.33 |
| 287.881 | 290.342 | 159.76 | 7.14 |
| 292.803 | 295.277 | 162.52 | 8.06 |
| 297.751 | 300.231 | 165.56 | 9.17 |
| 302.710 | 305.186 | 168.72 | 10.32 |

(Continued)

Table 10. Heat Capacity of Ethanol + n-Heptane (Continued)

$x_a = 0.8107$

(Sample weight in vacuo = 113.363 gms.)

| Initial Temp. K | Mean Temp. K | Heat Capacity Joules/gm. mole-K | Excess Heat Capacity Joules/gm. mole-K |
|---|---|---|---|
| | | Series 2 | |
| 195.029 | 197.252 | 110.18 | -0.54 |
| 199.474 | 201.887 | 110.59 | -0.48 |
| 204.300 | 206.730 | 111.12 | -0.41 |
| 209.161 | 211.608 | 111.68 | -0.37 |
| 214.055 | 216.552 | 112.42 | -0.25 |
| 219.048 | 221.540 | 113.18 | -0.18 |
| 224.033 | 226.518 | 114.03 | -0.10 |
| 229.002 | 231.506 | 115.01 | 0.05 |
| 234.009 | 236.472 | 116.07 | 0.20 |
| 238.539 | 240.978 | 117.20 | 0.46 |
| 243.418 | 245.876 | 118.45 | 0.69 |
| 248.334 | 250.819 | 119.75 | 0.89 |
| 253.305 | 255.785 | 121.14 | 1.11 |
| 258.265 | 260.732 | 122.69 | 1.41 |
| 263.200 | 265.645 | 124.32 | 1.72 |
| 268.090 | 270.540 | 126.11 | 2.12 |
| 272.990 | 275.427 | 127.96 | 2.49 |
| | | Series 1 | |
| 273.242 | 275.609 | 127.82 | 2.30 |
| 277.975 | 280.385 | 129.79 | 2.75 |
| 282.795 | 285.205 | 131.91 | 3.25 |
| 287.614 | 290.031 | 134.05 | 3.68 |
| 292.447 | 294.877 | 136.51 | 4.33 |
| 297.307 | 299.734 | 139.17 | 5.10 |
| 302.162 | 304.588 | 141.69 | 5.62 |

Table 11. Heat Capacity Data in Polynomial Form

The polynomial

$$Y = A_0 + A_1 T + A_2 T^2 + \cdots + A_n T^n$$

where $Y = C_p$ (pure components) or $C_p^E$ (mixtures) in Joules/mole and T is on IPTS-68 was used to represent the data given in Tables 6 to 10.

| | n-Heptane | 2-Propanol | Ethanol |
|---|---|---|---|
| $A_0$ | 2.1711845O(03)* | 5.38206447(01) | 1.27616505(02) |
| $A_1$ | -3.78719509(01) | 7.92412193(-01) | -6.86929771(-01) |
| $A_2$ | 2.91438270(-01) | -4.56017218(-03) | 4.20732978(-03) |
| $A_3$ | -1.12786214(-03) | 1.01887619(-05) | -1.18636754(-05) |
| $A_4$ | 2.20037134(-06) | 0 | 1.64216024(-08) |
| $A_5$ | -1.72199837(-09) | 0 | 0 |
| Standard Deviation | 0.163 | 0.059 | 0.044 |

| | 2-Propanol(1) + n-Heptane(2) | | |
|---|---|---|---|
| $x_1$ | 0.0809 | 0.2492 | 0.4219 |
| $A_0$ | -2.81177863(02) | -1.40298177(02) | -2.87023793(02) |
| $A_1$ | 4.92554808 | 2.27381586 | 4.87000564 |
| $A_2$ | -3.19302559(-02) | -1.37373090(-02) | -3.10316058(-02) |
| $A_3$ | 9.02147092(-05) | 3.60292490(-05) | 8.70180499(-05) |
| $A_4$ | -9.22774816(-08) | -3.25754788(-08) | -8.82595422(-08) |
| Standard Deviation | 0.058 | 0.068 | 0.070 |

*Numbers in parenthesis indicate multiplication by 10 raised to this power.

(Continued)

Table 11. Heat Capacity Data in Polynomial Form (Continued)

| 2-Propanol(1) + n-Heptane(2) | | | |
|---|---|---|---|
| $x_1$ | 0.5993 | 0.7984 | |
| $A_0$ | -3.62720221(02) | -2.92749990(02) | |
| $A_1$ | 6.13189826 | 4.82376173 | |
| $A_2$ | -3.88439089(-02) | -2.97301111(-02) | |
| $A_3$ | 1.08111347(-04) | 8.03490009(-05) | |
| $A_4$ | -1.09359208(-07) | -7.89131808(-08) | |
| Standard Deviation | 0.054 | 0.054 | |

| Ethanol(1) + n-Heptane(2) | | | |
|---|---|---|---|
| $x_1$ | 0.1023 | 0.2805 | 0.4388 |
| $A_0$ | -5.09012102(01) | 5.34472415(02) | 1.64198257(02) |
| $A_1$ | 9.71539805(-01) | -7.98680515 | -2.43951543 |
| $A_2$ | -6.63529268(-03) | 4.47591947(-02) | 1.37922424(-02) |
| $A_3$ | 1.87186816(-05) | -1.12510524(-04) | -3.61723022(-05) |
| $A_4$ | -1.70707910(-08) | 1.09066918(-07) | 3.88603291(-08) |
| Standard Deviation | 0.072 | 0.059 | 0.063 |

(Continued)

Table 11. Heat Capacity Data in Polynomial Form (Continued)

| Ethanol(1) + n-Heptane(2) | | |
|---|---|---|
| $x_1$ | 0.6140 | 0.8107 |
| $A_0$ | 3.28453065(02) | 1.46300110(02) |
| $A_1$ | -5.15703732 | -2.43726649 |
| $A_2$ | 3.04534594(-02) | 1.51700060(-02) |
| $A_3$ | -8.09492103(-05) | -4.23659537(-05) |
| $A_4$ | 8.30337049(-08) | 4.54890881(-08) |
| Standard Deviation | 0.053 | 0.064 |

Table 12. Heat Capacity Data of Pure Components in Polynomial Form on the IPKS-54

The polynomial

$$C_p = A_0 + A_1 T + A_2 T^2 + \cdots + A_n T^n$$

was used to represent the experimental heat capacity on the IPKS-54. The units of $C_p$ are cal./gm. mole-K, and the units of IPKS-54 are degrees Kelvin.

| | n-Heptane | 2-Propanol | Ethanol |
|---|---|---|---|
| $A_0$ | 4.49152519(02)* | 1.34753011(01) | 3.02774519(01) |
| $A_1$ | -7.56453655 | 1.83874957(-01) | -1.58639327(-01) |
| $A_2$ | 5.71157977(-02) | -1.07576157(-03) | 9.67746138(-04) |
| $A_3$ | -2.17196051(-04) | 2.42629718(-06) | -2.74367333(-06) |
| $A_4$ | 4.17411158(-07) | 0 | 3.86061974(-09) |
| $A_5$ | -3.22264250(-10) | 0 | 0 |
| Standard Deviation | 0.039 | 0.014 | 0.046 |

*Numbers in parenthesis indicate multiplication by 10 raised to this power.

Table 13. Comparison of the Heat Capacity of 2-Propanol

| T, IPKS-54 K | A* cal./gm. mole-K | B** cal./gm. mole-K | A - B cal./gm. mole-K |
|---|---|---|---|
| 188.32 | 26.156 | 26.108 | 0.048 |
| 191.18 | 26.264 | 26.304 | -0.040 |
| 192.50 | 26.315 | 26.356 | -0.041 |
| 196.28 | 26.469 | 26.487 | -0.018 |
| 197.13 | 26.505 | 26.529 | -0.024 |
| 201.27 | 26.688 | 26.733 | -0.045 |
| 202.03 | 26.723 | 26.754 | -0.031 |
| 206.29 | 26.927 | 26.954 | -0.027 |
| 207.06 | 26.966 | 27.055 | -0.089 |
| 212.23 | 27.238 | 27.300 | -0.062 |
| 216.20 | 27.465 | 27.487 | -0.022 |
| 216.93 | 27.508 | 27.510 | -0.002 |
| 221.18 | 27.771 | 27.809 | -0.038 |
| 220.01 | 27.825 | 27.846 | -0.021 |
| 226.22 | 28.108 | 28.199 | -0.091 |
| 227.04 | 28.165 | 28.189 | -0.024 |
| 231.21 | 28.470 | 28.506 | -0.036 |
| 231.99 | 28.529 | 28.538 | -0.009 |
| 236.14 | 28.857 | 28.904 | -0.047 |
| 237.06 | 28.933 | 28.938 | -0.005 |
| 242.23 | 29.379 | 29.375 | 0.004 |
| 247.34 | 29.857 | 29.842 | 0.015 |
| 251.26 | 30.248 | 30.243 | 0.005 |
| 252.39 | 30.365 | 30.344 | 0.021 |
| 256.27 | 30.782 | 30.782 | 0.000 |
| 257.37 | 30.905 | 30.871 | 0.034 |
| 261.07 | 31.332 | 31.352 | -0.020 |
| 262.30 | 31.478 | 31.468 | 0.010 |
| 265.96 | 31.930 | 31.909 | 0.021 |
| 267.17 | 32.084 | 32.062 | 0.022 |
| 270.78 | 32.560 | 32.585 | -0.025 |
| 271.98 | 32.723 | 32.627 | 0.096 |
| 275.35 | 33.196 | 33.171 | 0.025 |
| 276.81 | 33.407 | 33.453 | -0.045 |
| 280.06 | 33.892 | 33.855 | 0.037 |
| 281.80 | 34.160 | 34.180 | -0.020 |

* Heat capacity calculated from the polynomial given in Table 12, Appendix B.

** Experimental heat capacity data measured by Andon, et al.[1]

(Continued)

Table 13. Comparison of the Heat Capacity of 2-Propanol (Continued)

| T, IPKS-54 K | A* cal./gm. mole-K | B** cal./gm. mole-K | A - B cal./gm. mole-K |
|---|---|---|---|
| 284.70 | 34.619 | 34.607 | 0.012 |
| 286.86 | 34.972 | 34.990 | -0.018 |
| 289.28 | 35.379 | 35.370 | 0.009 |
| 290.32 | 35.558 | 35.559 | -0.001 |
| 293.80 | 36.171 | 36.181 | -0.010 |
| 295.38 | 36.459 | 36.552 | -0.093 |
| 298.23 | 36.990 | 36.950 | 0.042 |
| 299.20 | 37.175 | 37.096 | 0.079 |
| 299.96 | 37.322 | 37.253 | 0.069 |
| 302.57 | 37.834 | 37.872 | -0.038 |
| 303.46 | 38.012 | 37.968 | 0.044 |
| 304.27 | 38.176 | 38.111 | 0.065 |

Table 14. Comparison of the Heat Capacity of Ethanol

| T, IPKS-54 K | A* cal./gm. mole-K | B** cal./gm. mole-K | A - B cal./gm. mole-K |
|---|---|---|---|
| 165.311 | 20.987 | 21.016 | -0.029 |
| 168.537 | 21.010 | 21.039 | -0.029 |
| 171.848 | 21.038 | 21.072 | -0.034 |
| 175.040 | 21.070 | 21.104 | -0.034 |
| 179.857 | 21.127 | 21.160 | -0.033 |
| 183.109 | 21.172 | 21.206 | -0.034 |
| 186.365 | 21.222 | 21.257 | -0.035 |
| 189.624 | 21.277 | 21.309 | -0.032 |
| 192.808 | 21.336 | 21.372 | -0.036 |
| 195.969 | 21.399 | 21.434 | -0.035 |
| 204.932 | 21.605 | 21.636 | -0.031 |
| 208.063 | 21.687 | 21.712 | -0.025 |
| 211.181 | 21.773 | 21.792 | -0.019 |
| 214.358 | 21.866 | 21.889 | -0.023 |
| 217.496 | 21.963 | 21.985 | -0.022 |
| 220.589 | 22.064 | 22.080 | -0.016 |
| 228.576 | 22.351 | 22.367 | -0.016 |
| 231.808 | 22.477 | 22.510 | -0.033 |
| 235.051 | 22.610 | 22.636 | -0.026 |
| 238.290 | 22.750 | 22.783 | -0.033 |
| 241.590 | 22.899 | 22.935 | -0.036 |
| 244.738 | 23.048 | 23.075 | -0.027 |
| 247.756 | 23.197 | 23.232 | -0.035 |
| 250.890 | 23.359 | 23.390 | -0.031 |
| 253.977 | 23.525 | 23.564 | -0.039 |
| 257.007 | 23.695 | 23.730 | -0.035 |
| 260.063 | 23.874 | 23.908 | -0.034 |
| 263.361 | 24.075 | 24.113 | -0.038 |
| 266.963 | 24.305 | 24.341 | -0.036 |
| 270.623 | 24.549 | 24.604 | -0.055 |
| 274.272 | 24.805 | 24.867 | -0.062 |
| 277.116 | 25.012 | 25.049 | -0.037 |
| 280.557 | 25.273 | 25.326 | -0.053 |
| 284.026 | 25.548 | 25.601 | -0.053 |
| 287.363 | 25.824 | 25.873 | -0.049 |
| 290.722 | 26.113 | 26.174 | -0.061 |
| 294.075 | 26.413 | 26.462 | -0.049 |

* Heat capacity calculated from the polynomial given in Table 12, Appendix B.

** Experimental heat capacity data measured by Hwa.[21]

(Continued)

Table 14. Comparison of the Heat Capacity of Ethanol (Continued)

| T, IPKS-54 K | A* cal./gm. mole-K | B** cal./gm. mole-K | A - B cal./gm. mole-K |
|---|---|---|---|
| 297.359 | 26.719 | 26.782 | -0.063 |
| 297.148 | 26.699 | 26.752 | -0.053 |
| 301.087 | 26.082 | 27.145 | -0.063 |
| 304.204 | 27.398 | 27.473 | -0.075 |

Table 15. Comparisons of Heat Capacity Data of n-Heptane to the Selected Values of the U. S. Bureau of Mines.*

| | Deviations. $C_{sat}$ (exp.) - $C_{sat}$ (sel.) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| T, IPKS-54 K | BM 1947 | BM 1949 | BM 1951A | BM 1951B | BM 1954 | NBS 1947 | NBS 1954 | Brown 1969 |
| 182.55 | 0.01 | 0.04 | 0.01 | 0.01 | -0.02 | - | 0.03 | 0.01 |
| 185 | 0.02 | 0.03 | 0.00 | 0.01 | -0.01 | - | -0.01 | -0.03 |
| 190 | 0.04 | 0.01 | 0.00 | 0.00 | 0.01 | - | -0.02 | -0.07 |
| 195 | 0.03 | 0.00 | -0.01 | 0.00 | 0.01 | - | -0.03 | -0.09 |
| 200 | 0.00 | -0.01 | -0.01 | -0.01 | 0.01 | - | -0.04 | -0.11 |
| 205 | 0.00 | -0.02 | -0.01 | -0.01 | 0.01 | - | -0.04 | -0.11 |
| 210 | 0.02 | -0.01 | -0.01 | -0.01 | 0.02 | - | -0.03 | -0.11 |
| 215 | 0.02 | -0.00 | -0.01 | -0.01 | 0.02 | - | -0.03 | -0.11 |
| 220 | 0.03 | -0.01 | -0.01 | -0.01 | 0.02 | - | -0.03 | -0.11 |
| 225 | 0.02 | -0.01 | 0.00 | 0.00 | 0.01 | - | -0.04 | -0.10 |
| 230 | 0.02 | 0.00 | 0.02 | 0.00 | 0.00 | - | -0.04 | -0.10 |
| 235 | 0.01 | 0.00 | 0.03 | 0.00 | 0.00 | - | -0.04 | -0.10 |
| 240 | 0.01 | 0.00 | 0.03 | -0.01 | 0.01 | - | -0.03 | -0.10 |
| 245 | -0.01 | -0.01 | 0.03 | -0.02 | 0.00 | - | -0.04 | -0.11 |
| 250 | -0.02 | -0.02 | 0.02 | -0.03 | 0.00 | - | -0.04 | -0.11 |
| 255 | -0.03 | -0.01 | 0.03 | -0.05 | 0.00 | - | -0.05 | -0.12 |
| 260 | -0.04 | -0.01 | 0.01 | -0.05 | 0.00 | - | -0.06 | -0.12 |
| 265 | -0.04 | -0.01 | 0.01 | -0.04 | 0.01 | - | -0.06 | -0.12 |
| 270 | -0.04 | 0.00 | 0.01 | -0.03 | 0.01 | - | -0.05 | -0.11 |
| 275 | -0.05 | 0.00 | 0.02 | -0.03 | 0.01 | - | -0.03 | -0.10 |
| 280 | -0.05 | -0.01 | 0.01 | 0.05 | 0.01 | -0.02 | -0.03 | -0.10 |
| 285 | -0.05 | -0.01 | 0.01 | -0.07 | 0.01 | -0.02 | -0.04 | -0.10 |
| 290 | -0.04 | -0.02 | 0.01 | -0.08 | 0.00 | -0.02 | -0.04 | -0.10 |
| 295 | -0.04 | -0.01 | 0.02 | -0.08 | 0.00 | -0.02 | -0.05 | -0.08 |
| 298.15 | -0.05 | -0.01 | 0.01 | -0.09 | 0.00 | -0.02 | -0.05 | -0.08 |
| 300 | -0.06 | -0.01 | 0.01 | -0.09 | -0.01 | -0.02 | -0.05 | -0.08 |

* See reference 34 for the selected values.

# APPENDIX C

## DERIVED EXCESS THERMODYNAMIC PROPERTIES

Table 16. Derived Excess Thermodynamic Properties of 2-Propanol + n-Heptane

| $x_a$ | 0.0809 | 0.2492 | 0.4219 | 0.5993 | 0.7984 |
|---|---|---|---|---|---|
| T,K | Excess Heat Capacity (Joules/gm. mole-K) | | | | |
| 318.15 | 13.69 | 19.13 | 19.35 | 17.46 | 11.65 |
| 313.15 | 13.06 | 17.77 | 18.42 | 16.63 | 10.92 |
| 308.15 | 12.36 | 16.45 | 17.43 | 15.71 | 10.17 |
| *303.15 | 11.61 | 15.19 | 16.38 | 14.73 | 9.39 |
| 298.15 | 10.82 | 13.97 | 15.32 | 13.71 | 8.60 |
| 293.15 | 10.00 | 12.82 | 14.24 | 12.67 | 7.82 |
| 288.15 | 9.18 | 11.72 | 13.16 | 11.62 | 7.05 |
| 283.15 | 8.36 | 10.68 | 12.09 | 10.58 | 6.30 |
| 278.15 | 7.55 | 9.70 | 11.04 | 9.55 | 5.58 |
| 273.15 | 6.77 | 8.78 | 10.02 | 8.55 | 4.89 |
| 268.15 | 6.03 | 7.92 | 9.04 | 7.60 | 4.24 |
| 263.15 | 5.33 | 7.11 | 8.11 | 6.69 | 3.63 |
| 258.15 | 4.67 | 6.37 | 7.22 | 5.83 | 3.07 |
| 253.15 | 4.07 | 5.69 | 6.39 | 5.04 | 2.56 |
| 248.15 | 3.52 | 5.06 | 5.61 | 4.30 | 2.09 |
| 243.15 | 3.03 | 4.48 | 4.89 | 3.62 | 1.67 |
| 238.15 | 2.59 | 3.95 | 4.23 | 3.01 | 1.29 |
| 233.15 | 2.21 | 3.47 | 3.62 | 2.45 | 0.96 |
| 228.15 | 1.89 | 3.03 | 3.07 | 1.95 | 0.66 |
| 223.15 | 1.61 | 2.62 | 2.56 | 1.50 | 0.39 |
| 218.15 | 1.38 | 2.25 | 2.10 | 1.09 | 0.15 |
| 213.15 | 1.18 | 1.91 | 1.67 | 0.72 | -0.08 |
| 208.15 | 1.02 | 1.58 | 1.26 | 0.37 | -0.30 |
| 203.15 | 0.88 | 1.28 | 0.88 | 0.03 | -0.52 |
| 198.15 | 0.74 | 0.98 | 0.50 | -0.31 | -0.76 |

* Values above this temperature are obtained by extrapolating the polynomials given in Table 11, Appendix B.

(Continued)

Table 16. Derived Excess Thermodynamic Properties of 2-Propanol + n-Heptane (Continued)

| $x_a$ | 0.0809 | 0.2492 | 0.4219 | 0.5993 | 0.7984 |
|---|---|---|---|---|---|
| T,K | Excess Heat Capacity (Joules/gm.. mole-K) | | | | |
| 193.15 | 0.62 | 0.67 | 0.12 | -0.67 | -1.03 |
| 188.15 | 0.46 | 0.37 | -0.28 | -1.06 | -1.34 |
| **183.15 | 0.28 | 0.04 | -0.71 | -1.50 | -1.71 |
| 178.15 | 0.05 | -0.31 | -1.19 | -2.02 | -2.15 |
| 173.15 | -0.24 | -0.69 | -1.74 | -2.63 | -2.68 |
| 168.15 | -0.62 | -1.11 | -2.38 | -3.36 | -3.32 |
| 163.15 | -1.09 | -1.60 | -3.12 | -4.23 | -4.09 |

** Values below this temperature are obtained by extrapolating the polynomials given in Table 11, Appendix B.

(Continued)

Table 16. Derived Excess Thermodynamic Properties of 2-Propanol + n-Heptane (Continued)

| $x_a$ | 0.0809 | 0.2492 | 0.4219 | 0.5993 | 0.7984 |
|---|---|---|---|---|---|
| T,K | Excess Enthalpy (Joules/gm. mole) | | | | |
| 318.15 | 748 | 1101 | 1179 | 1051 | 664 |
| 313.15 | 682 | 1009 | 1084 | 966 | 608 |
| 308.15 | 618 | 923 | 995 | 885 | 555 |
| *303.15 | (558)*** | (844) | (910) | (809) | (506) |
| 298.15 | 502 | 771 | 831 | 738 | 461 |
| 293.15 | 450 | 704 | 757 | 672 | 420 |
| 288.15 | 402 | 643 | 688 | 611 | 383 |
| 283.15 | 358 | 587 | 625 | 556 | 349 |
| 278.15 | 318 | 536 | 567 | 505 | 320 |
| 273.15 | 283 | 490 | 515 | 460 | 294 |
| 268.15 | 251 | 448 | 467 | 420 | 271 |
| 263.15 | 222 | 411 | 424 | 384 | 251 |
| 258.15 | 197 | 377 | 386 | 353 | 234 |
| 253.15 | 175 | 347 | 352 | 326 | 220 |
| 248.15 | 156 | 320 | 322 | 302 | 209 |
| 243.15 | 140 | 296 | 296 | 283 | 199 |
| 238.15 | 126 | 275 | 273 | 266 | 192 |
| 233.15 | 114 | 257 | 253 | 252 | 186 |
| 228.15 | 104 | 240 | 236 | 241 | 182 |
| 223.15 | 95.2 | 226 | 222 | 233 | 180 |
| 218.15 | 87.7 | 214 | 211 | 226 | 178 |
| 213.15 | 81.3 | 204 | 201 | 222 | 178 |
| 208.15 | 75.8 | 195 | 194 | 219 | 179 |
| 203.15 | 71.1 | 188 | 189 | 218 | 181 |
| 198.15 | 67.0 | 182 | 185 | 219 | 184 |
| 193.15 | 63.6 | 178 | 184 | 221 | 189 |
| 188.15 | 60.9 | 175 | 184 | 225 | 195 |
| **183.15 | 59.1 | 174 | 187 | 232 | 202 |
| 178.15 | 58.2 | 175 | 191 | 241 | 212 |
| 173.15 | 58.6 | 178 | 199 | 252 | 224 |
| 168.15 | 60.7 | 182 | 209 | 267 | 239 |
| 163.15 | 65.0 | 189 | 223 | 286 | 257 |

*** Integration constants

(Continued)

Table 16. Derived Excess Thermodynamic Properties of 2-Propanol + n-Heptane (Continued)

| $x_a$ | 0.0809 | 0.2492 | 0.4219 | 0.5993 | 0.7984 |
|---|---|---|---|---|---|
| T,K | Excess Gibbs Free Energy (Joules/gm. mole) | | | | |
| 318.15 | 504 | 1048 | 1262 | 1215 | 823 |
| 313.15 | 507 | 1048 | 1259 | 1211 | 820 |
| 308.15 | 510 | 1047 | 1256 | 1207 | 817 |
| *303.15 | (511)*** | (1044) | (1251) | (1201) | (812) |
| 298.15 | 511 | 1040 | 1245 | 1194 | 807 |
| 293.15 | 511 | 1035 | 1237 | 1186 | 800 |
| 288.15 | 509 | 1029 | 1228 | 1176 | 794 |
| 283.15 | 507 | 1022 | 1218 | 1166 | 786 |
| 278.15 | 504 | 1013 | 1207 | 1155 | 778 |
| 273.15 | 500 | 1004 | 1195 | 1143 | 770 |
| 268.15 | 496 | 995 | 1183 | 1130 | 761 |
| 263.15 | 491 | 984 | 1169 | 1116 | 751 |
| 258.15 | 486 | 973 | 1154 | 1102 | 742 |
| 253.15 | 480 | 961 | 1139 | 1087 | 732 |
| 248.15 | 474 | 949 | 1123 | 1072 | 722 |
| 243.15 | 467 | 936 | 1107 | 1056 | 711 |
| 238.15 | 460 | 922 | 1090 | 1040 | 701 |
| 233.15 | 453 | 909 | 1072 | 1024 | 690 |
| 228.15 | 446 | 894 | 1055 | 1007 | 679 |
| 223.15 | 438 | 880 | 1037 | 990 | 668 |
| 218.15 | 430 | 865 | 1018 | 973 | 657 |
| 213.15 | 423 | 850 | 1000 | 956 | 646 |
| 208.15 | 414 | 835 | 981 | 939 | 635 |
| 203.15 | 406 | 819 | 962 | 922 | 624 |
| 198.15 | 398 | 804 | 943 | 904 | 613 |
| 193.15 | 390 | 788 | 924 | 887 | 603 |
| 188.15 | 381 | 772 | 904 | 870 | 592 |
| **183.15 | 373 | 756 | 885 | 853 | 582 |
| 178.15 | 364 | 740 | 866 | 836 | 571 |
| 173.15 | 355 | 725 | 848 | 819 | 561 |
| 168.15 | 347 | 709 | 829 | 803 | 552 |
| 163.15 | 338 | 693 | 811 | 787 | 543 |

*** Integration constants

(Continued)

Table 16. Derived Excess Thermodynamic Properties of 2-Propanol + n-Heptane (Continued)

| $x_a$ | 0.0809 | 0.2492 | 0.4219 | 0.5993 | 0.7984 |
|---|---|---|---|---|---|
| T,K | Excess Entropy (Joules/gm. mole-K) | | | | |
| 318.15 | 0.768 | 0.167 | -0.260 | -0.514 | -0.501 |
| 313.15 | 0.556 | -0.126 | -0.560 | -0.784 | -0.680 |
| 308.15 | 0.351 | -0.401 | -0.848 | -1.044 | -0.849 |
| *303.15 | 0.155 | -0.660 | -1.125 | -1.293 | -1.009 |
| 298.15 | -0.031 | -0.902 | -1.389 | -1.530 | -1.159 |
| 293.15 | -0.207 | -1.129 | -1.639 | -1.753 | -1.298 |
| 288.15 | -0.372 | -1.340 | -1.874 | -1.962 | -1.426 |
| 283.15 | -0.526 | -1.535 | -2.095 | -2.156 | -1.542 |
| 278.15 | -0.668 | -1.717 | -2.301 | -2.335 | -1.648 |
| 273.15 | -0.797 | -1.884 | -2.492 | -2.499 | -1.743 |
| 268.15 | -0.916 | -2.038 | -2.668 | -2.648 | -1.827 |
| 263.15 | -1.022 | -2.180 | -2.830 | -2.783 | -1.901 |
| 258.15 | -1.118 | -2.309 | -2.977 | -2.903 | -1.965 |
| 253.15 | -1.203 | -2.427 | -3.110 | -3.009 | -2.020 |
| 248.15 | -1.279 | -2.534 | -3.229 | -3.102 | -2.067 |
| 243.15 | -1.345 | -2.631 | -3.336 | -3.182 | -2.105 |
| 238.15 | -1.404 | -2.718 | -3.431 | -3.251 | -2.135 |
| 233.15 | -1.455 | -2.797 | -3.514 | -3.309 | -2.159 |
| 228.15 | -1.499 | -2.867 | -3.586 | -3.357 | -2.177 |
| 223.15 | -1.537 | -2.929 | -3.649 | -3.395 | -2.188 |
| 218.15 | -1.571 | -2.985 | -3.701 | -3.424 | -2.194 |
| 213.15 | -1.601 | -3.033 | -3.745 | -3.445 | -2.195 |
| 208.15 | -1.627 | -3.074 | -3.779 | -3.458 | -2.191 |
| 203.15 | -1.650 | -3.109 | -3.805 | -3.463 | -2.181 |
| 198.15 | -1.670 | -3.137 | -3.823 | -3.460 | -2.165 |
| 193.15 | -1.688 | -3.158 | -3.831 | -3.447 | -2.142 |
| 188.15 | -1.702 | -3.172 | -3.829 | -3.425 | -2.111 |
| **183.15 | -1.712 | -3.177 | -3.815 | -3.390 | -2.070 |
| 178.15 | -1.717 | -3.173 | -3.789 | -3.342 | -2.017 |
| 173.15 | -1.714 | -3.159 | -3.747 | -3.276 | -1.949 |
| 168.15 | -1.702 | -3.133 | -3.687 | -3.188 | -1.861 |
| 163.15 | -1.676 | -3.092 | -3.604 | -3.074 | -1.750 |

Table 17. Derived Excess Thermodynamic Properties of Ethanol + n-Heptane

| $x_a$ | 0.1023 | 0.2805 | 0.4388 | 0.6140 | 0.8107 |
|---|---|---|---|---|---|
| T,K | Excess Heat Capacity (Joules/gm. mole-K) | | | | |
| 318.15 | 14.47 | 18.23 | 17.39 | 14.13 | 8.13 |
| 313.15 | 13.32 | 16.43 | 15.67 | 12.54 | 7.13 |
| 308.15 | 12.22 | 14.79 | 14.08 | 11.12 | 6.25 |
| *303.15 | 11.16 | 13.29 | 12.62 | 9.84 | 5.45 |
| 298.15 | 10.15 | 11.92 | 11.28 | 8.69 | 4.75 |
| 293.15 | 9.19 | 10.67 | 10.04 | 7.66 | 4.12 |
| 288.15 | 8.28 | 9.52 | 8.90 | 6.73 | 3.56 |
| 283.15 | 7.42 | 8.47 | 7.86 | 5.89 | 3.06 |
| 278.15 | 6.62 | 7.49 | 6.91 | 5.14 | 2.62 |
| 273.15 | 5.87 | 6.59 | 6.03 | 4.46 | 2.22 |
| 268.15 | 5.17 | 5.76 | 5.24 | 3.84 | 1.86 |
| 263.15 | 4.52 | 5.00 | 4.52 | 3.28 | 1.54 |
| 258.15 | 3.93 | 4.30 | 3.86 | 2.78 | 1.25 |
| 253.15 | 3.39 | 3.66 | 3.28 | 2.32 | 0.99 |
| 248.15 | 2.90 | 3.08 | 2.75 | 1.91 | 0.75 |
| 243.15 | 2.46 | 2.57 | 2.29 | 1.54 | 0.53 |
| 238.15 | 2.07 | 2.13 | 1.89 | 1.21 | 0.33 |
| 233.15 | 1.72 | 1.76 | 1.54 | 0.93 | 0.16 |
| 228.15 | 1.42 | 1.47 | 1.26 | 0.69 | -0.00 |
| 223.15 | 1.16 | 1.28 | 1.03 | 0.51 | -0.14 |
| 218.15 | 0.94 | 1.18 | 0.86 | 0.37 | -0.26 |
| **213.15 | 0.76 | 1.20 | 0.76 | 0.30 | -0.36 |
| 208.15 | 0.61 | 1.35 | 0.71 | 0.29 | -0.44 |
| 203.15 | 0.49 | 1.64 | 0.73 | 0.36 | -0.48 |
| 198.15 | 0.40 | 2.09 | 0.82 | 0.51 | -0.50 |
| 193.15 | 0.33 | 2.72 | 0.99 | 0.76 | -0.48 |
| 188.15 | 0.29 | 3.54 | 1.23 | 1.11 | -0.42 |
| 183.15 | 0.25 | 4.59 | 1.55 | 1.58 | -0.32 |

* Values above this temperature are obtained by extrapolating the polynomials given in Table 11, Appendix B.

** Values below this temperature are obtained by extrapolating the polynomials given in Table 11, Appendix B.

(Continued)

Table 17. Derived Excess Thermodynamic Properties of Ethanol + n-Heptane (Continued)

| $x_a$ | 0.1023 | 0.2805 | 0.4388 | 0.6140 | 0.8107 |
|---|---|---|---|---|---|
| T,K | Excess Enthalpy (Joules/gm. mole) | | | | |
| 318.15 | 699 | 899 | 894 | 771 | 509 |
| 313.15 | 629 | 812 | 811 | 704 | 471 |
| 308.15 | 565 | 734 | 737 | 645 | 437 |
| *303.15 | (507)*** | (664) | (670) | (593) | (408) |
| 298.15 | 454 | 601 | 610 | 547 | 383 |
| 293.15 | 405 | 545 | 557 | 506 | 360 |
| 288.15 | 362 | 494 | 510 | 470 | 341 |
| 283.15 | 323 | 449 | 468 | 439 | 325 |
| 278.15 | 287 | 409 | 431 | 411 | 310 |
| 273.15 | 256 | 374 | 399 | 387 | 298 |
| 268.15 | 229 | 343 | 371 | 366 | 288 |
| 263.15 | 205 | 316 | 346 | 348 | 280 |
| 258.15 | 183 | 293 | 325 | 333 | 273 |
| 253.15 | 165 | 273 | 307 | 321 | 267 |
| 248.15 | 149 | 257 | 292 | 310 | 263 |
| 243.15 | 136 | 242 | 280 | 302 | 260 |
| 238.15 | 125 | 231 | 269 | 294 | 257 |
| 233.15 | 115 | 221 | 261 | 289 | 256 |
| 228.15 | 108 | 213 | 254 | 285 | 256 |
| 223.15 | 101 | 206 | 248 | 282 | 256 |
| 218.15 | 95.9 | 200 | 243 | 280 | 257 |
| **213.15 | 91.6 | 194 | 239 | 278 | 259 |
| 208.15 | 88.2 | 188 | 236 | 277 | 261 |
| 203.15 | 85.4 | 180 | 232 | 275 | 263 |
| 198.15 | 83.3 | 171 | 228 | 273 | 266 |
| 293.15 | 81.4 | 159 | 223 | 270 | 268 |
| 188.15 | 79.9 | 144 | 218 | 266 | 270 |
| 183.15 | 78.5 | 123 | 211 | 259 | 272 |

*** Integration constants

(Continued)

Table 17. Derived Excess Thermodynamic Properties of Ethanol + n-Heptane (Continued)

| $x_a$ | 0.1023 | 0.2805 | 0.4388 | 0.6140 | 0.8107 |
|---|---|---|---|---|---|
| T,K | Excess Gibbs Freee Energy (Joules/gm. mole) | | | | |
| 318.15 | 673 | 1283 | 1481 | 1387 | 938 |
| 313.15 | 672 | 1276 | 1471 | 1376 | 931 |
| 308.15 | 671 | 1268 | 1460 | 1365 | 923 |
| *303.15 | (669)*** | (1259) | (1448) | (1353) | (915) |
| 298.15 | 666 | 1249 | 1435 | 1340 | 906 |
| 293.15 | 662 | 1237 | 1420 | 1326 | 897 |
| 288.15 | 657 | 1225 | 1405 | 1312 | 888 |
| 283.15 | 652 | 1212 | 1389 | 1297 | 878 |
| 278.15 | 646 | 1198 | 1373 | 1282 | 869 |
| 273.15 | 639 | 1184 | 1355 | 1266 | 858 |
| 268.15 | 632 | 1169 | 1338 | 1250 | 848 |
| 263.15 | 624 | 1153 | 1319 | 1233 | 838 |
| 258.15 | 616 | 1137 | 1301 | 1216 | 827 |
| 253.15 | 607 | 1120 | 1282 | 1199 | 816 |
| 248.15 | 598 | 1103 | 1262 | 1181 | 805 |
| 243.15 | 589 | 1086 | 1243 | 1164 | 794 |
| 238.15 | 580 | 1069 | 1223 | 1146 | 783 |
| 233.15 | 570 | 1051 | 1203 | 1128 | 772 |
| 228.15 | 560 | 1033 | 1182 | 1110 | 761 |
| 223.15 | 550 | 1015 | 1162 | 1092 | 750 |
| 218.15 | 540 | 997 | 1141 | 1074 | 739 |
| **213.15 | 530 | 978 | 1121 | 1055 | 728 |
| 208.15 | 519 | 960 | 1100 | 1037 | 717 |
| 203.15 | 509 | 941 | 1079 | 1019 | 706 |
| 198.15 | 499 | 923 | 1058 | 1001 | 695 |
| 193.15 | 488 | 903 | 1037 | 982 | 684 |
| 188.15 | 478 | 884 | 1016 | 964 | 674 |
| 183.15 | 467 | 864 | 995 | 945 | 663 |

*** Integration constants

(Continued)

Table 17. Derived Excess Thermodynamic Properties of Ethanol + n-Heptane (Continued)

| $x_a$ | 0.1023 | 0.2805 | 0.4388 | 0.6140 | 0.8107 |
|---|---|---|---|---|---|
| T,K | Excess Entropy (Joules/gm. mole-K) | | | | |
| 318.15 | 0.082 | -1.208 | -1.847 | -1.935 | -1.349 |
| 313.15 | -0.138 | -1.482 | -2.108 | -2.146 | -1.469 |
| 308.15 | -0.343 | -1.733 | -2.348 | -2.336 | -1.577 |
| *303.15 | -0.534 | -1.963 | -2.566 | -2.507 | -1.672 |
| 298.15 | -0.711 | -2.172 | -2.765 | -2.661 | -1.757 |
| 293.15 | -0.875 | -2.363 | -2.945 | -2.799 | -1.832 |
| 288.15 | -1.025 | -2.537 | -3.108 | -2.922 | -1.898 |
| 283.15 | -1.162 | -2.694 | -3.254 | -3.033 | -1.956 |
| 278.15 | -1.287 | -2.836 | -3.386 | -3.131 | -2.007 |
| 273.15 | -1.400 | -2.964 | -3.503 | -3.217 | -2.050 |
| 268.15 | -1.502 | -3.078 | -3.607 | -3.294 | -2.088 |
| 263.15 | -1.593 | -3.179 | -3.699 | -3.361 | -2.120 |
| 258.15 | -1.674 | -3.268 | -3.779 | -3.419 | -2.147 |
| 253.15 | -1.746 | -3.345 | -3.849 | -3.469 | -2.168 |
| 248.15 | -1.808 | -3.413 | -3.909 | -3.511 | -2.186 |
| 243.15 | -1.863 | -3.470 | -3.960 | -3.546 | -2.199 |
| 238.15 | -1.910 | -3.519 | -4.003 | -3.574 | -2.208 |
| 233.15 | -1.950 | -3.560 | -4.039 | -3.597 | -2.213 |
| 228.15 | -1.984 | -3.594 | -4.070 | -3.615 | -2.214 |
| 223.15 | -2.012 | -3.625 | -4.095 | -3.628 | -2.213 |
| 218.15 | -2.036 | -3.652 | -4.116 | -3.638 | -2.208 |
| **213.15 | -2.056 | -3.680 | -4.135 | -3.645 | -2.201 |
| 208.15 | -2.071 | -3.710 | -4.152 | -3.652 | -2.191 |
| 203.15 | -2.085 | -3.746 | -4.170 | -3.660 | -2.180 |
| 198.15 | -2.096 | -3.792 | -4.290 | -3.671 | -2.168 |
| 193.15 | -2.105 | -3.853 | -4.212 | -3.687 | -2.155 |
| 188.15 | -2.113 | -3.935 | -4.241 | -3.711 | -2.143 |
| 183.15 | -2.121 | -4.044 | -4.278 | -3.747 | -2.133 |

Table 18. Derived Gibbs Free Energy of Mixing for 2-Propanol + n-Heptane

| $x_a$ | 0.0809 | 0.2492 | 0.4219 | 0.5993 | 0.7984 |
|---|---|---|---|---|---|
| T,K | Gibbs Free Energy of Mixing (Joules/gm. mole) | | | | |
| 318.15 | -239 | -437 | -540 | -566 | -506 |
| 313.15 | -224 | -414 | -513 | -542 | -488 |
| 308.15 | -210 | -392 | -489 | -518 | -471 |
| *303.15 | -197 | -371 | -465 | -496 | -455 |
| 298.15 | -185 | -352 | -443 | -475 | -439 |
| 293.15 | -174 | -333 | -422 | -455 | -425 |
| 288.15 | -164 | -316 | -403 | -437 | -411 |
| 283.15 | -154 | -300 | -385 | -419 | -397 |
| 278.15 | -146 | -285 | -367 | -402 | -384 |
| 273.15 | -138 | -271 | -351 | -386 | -372 |
| 268.15 | -130 | -257 | -336 | -371 | -360 |
| 263.15 | -123 | -244 | -321 | -357 | -348 |
| 258.15 | -117 | -232 | -307 | -343 | -337 |
| 253.15 | -111 | -221 | -294 | -330 | -326 |
| 248.15 | -106 | -210 | -282 | -317 | -315 |
| 243.15 | -101 | -199 | -270 | -305 | -305 |
| 238.15 | - 95.8 | -189 | -258 | -293 | -295 |
| 233.15 | - 91.3 | -180 | -247 | -281 | -285 |
| 228.15 | - 87.0 | -171 | -237 | -270 | -274 |
| 223.15 | - 82.9 | -162 | -227 | -259 | -264 |
| 218.15 | - 79.0 | -153 | -217 | -248 | -255 |
| 213.15 | - 75.3 | -145 | -207 | -237 | -245 |
| 208.15 | - 71.7 | -137 | -198 | -226 | -235 |
| 203.15 | - 68.2 | -129 | -188 | -216 | -225 |
| 198.15 | - 64.8 | -121 | -179 | -205 | -215 |
| 193.15 | - 61.5 | -114 | -170 | -194 | -205 |
| 188.15 | - 58.3 | -106 | -161 | -184 | -194 |
| **183.15 | - 55.2 | - 98.6 | -151 | -173 | -184 |
| 178.15 | - 52.1 | - 91.2 | -142 | -161 | -173 |
| 173.15 | - 59.0 | - 83.7 | -133 | -150 | -162 |
| 168.15 | - 45.9 | - 76.1 | -123 | -138 | -151 |
| 163.15 | - 42.6 | - 68.3 | -113 | -126 | -139 |

* Values above this temperature are obtained by extrapolating the polynomials given in Table 11, Appendix B.

** Values below this temperature are obtained by extrapolating the polynomials given in Table 11, Appendix B.

Table 19. Derived Gibbs Free Energy of Mixing for Ethanol + n-Heptane

| $x_a$ | 0.1023 | 0.2805 | 0.4388 | 0.6140 | 0.8107 |
|---|---|---|---|---|---|
| T,K | Gibbs Free Energy of Mixing (Joules/gm. mole) | | | | |
| 318.15 | -201 | -287 | -332 | -378 | -346 |
| 313.15 | -187 | -269 | -314 | -360 | -333 |
| 308.15 | -175 | -252 | -296 | -344 | -320 |
| *303.15 | -163 | -237 | -280 | -328 | -308 |
| 298.15 | -153 | -222 | -265 | -313 | -296 |
| 293.15 | -143 | -209 | -251 | -299 | -285 |
| 288.15 | -134 | -197 | -237 | -286 | -274 |
| 283.15 | -126 | -185 | -225 | -273 | -264 |
| 278.15 | -118 | -174 | -213 | -261 | -254 |
| 273.15 | -111 | -164 | -202 | -249 | -244 |
| 268.15 | -104 | -154 | -191 | -237 | -234 |
| 263.15 | - 98.5 | -145 | -181 | -226 | -224 |
| 258.15 | - 93.0 | -137 | -171 | -215 | -215 |
| 253.15 | - 87.8 | -129 | -161 | -205 | -205 |
| 248.15 | - 82.9 | -121 | -152 | -195 | -196 |
| 243.15 | - 78.4 | -113 | -143 | -185 | -187 |
| 238.15 | - 74.1 | -106 | -135 | -175 | -178 |
| 233.15 | - 70.0 | - 99.3 | -127 | -165 | -168 |
| 228.15 | - 66.2 | - 92.5 | -118 | -155 | -159 |
| 223.15 | - 62.4 | - 85.9 | -110 | -146 | -150 |
| 218.15 | - 58.8 | - 79.5 | -102 | -136 | -141 |
| **213.15 | - 55.3 | - 73.1 | - 94.3 | -126 | -132 |
| 208.15 | - 51.9 | - 66.9 | - 86.6 | -117 | -123 |
| 203.15 | - 48.6 | - 60.9 | - 78.9 | -108 | -114 |
| 198.15 | - 45.3 | - 55.1 | - 71.3 | - 98.1 | -104 |
| 193.15 | - 42.1 | - 49.5 | - 63.8 | - 88.8 | - 94.8 |
| 188.15 | - 38.9 | - 44.3 | - 56.4 | - 79.6 | - 85.4 |
| 183.15 | - 35.8 | - 39.5 | - 49.2 | - 70.5 | - 75.9 |

* Values above this temperature are obtained by extrapolating the polynomials given in Table 11, Appendix B.

** Values below this temperature are obtained by extrapolating the polynomials given in Table 11, Appendix B.

# APPENDIX D

## CALCULATION OF THE HEAT CAPACITY

### General

A heat capacity run involved an initial equilibrium temperature, a heating interval, and a final equilibrium temperature. The experimental data are

1. The initial resistances, R and N, were measured with a Mueller G-2 Bridge. The initial resistance of the platinum resistance thermometer was the arithmetic average $(N + R)/2$.

2. During the heating interval two readings of voltage were made using a White potentiometer. The voltage across the volt box, P, and the voltage across the standard resistor, Q, were the arithmetic average of the two pairs of measurements at approximately one-third and two-thirds of the total time of the heating period.

3. The total time, S, of the heating interval was recorded in seconds.

4. The final resistances, R and N were measured. The final resistance of the platinum resistance thermometer was $(N + R)/2$.

The heat capacity was calculated from these experimental data.

The temperatures corresponding to the resistance of steps 1 and 4 were calculated from the Callendar-Van Dusen equation. The equation relates the temperature on the International Practical Temperature Scale of 1948 to the resistance of the platinum resistance thermometer. The

equation was approximated by a fourth degree polynomial in resistance

$$t = A_0 + A_1 R + A_2 R^2 + A_3 R^3 + A_4 R^4$$

which gave an initial guess of temperature. An iterative solution of the Callendar-Van Dusen equation by the method of successive substitution yielded an equilibrium temperature. The iteration was stopped when $|t_n - t_{n-1}| \leq 0.0001$. This equilibrium temperature was converted to the IPTS 1968 using the polynomial given in Table 5 of Appendix A.

The amount of heat added to the calorimeter can plus sample was calculated using the data of steps 2 and 3. A schematic diagram of the heating circuit is shown in Figure 10. The total heat dissipated at the heater resistor is

$$\text{Heat} = \int_0^S E \cdot I \, d\tau \, .$$

Using the relations

$$I_T = I_S = I_H + I_{V.B.}$$

$$E_H = E_{V.B.} = f \cdot P$$

$$I_S = Q/R_S$$

$$I_{V.B.} = f\, P/R_{V.B.}$$

and assuming that f, P, Q, $R_S$, and $R_{V.B.}$ are independent of time over the heating interval, S, then

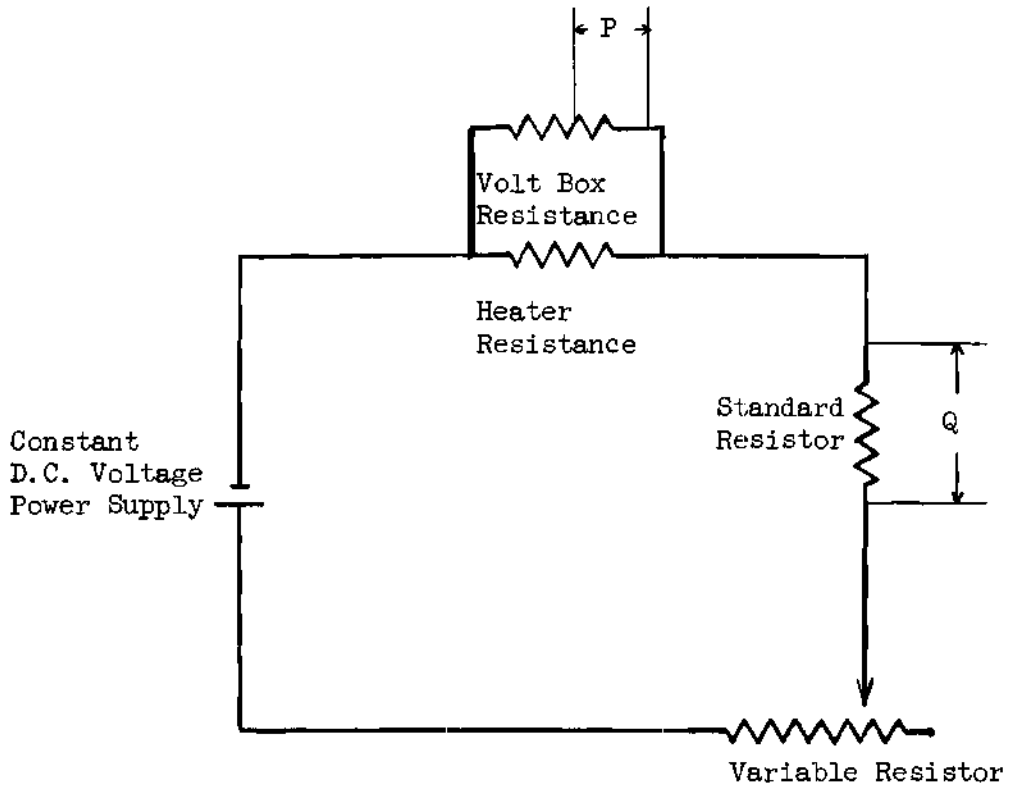


Figure 10. Heating Circuit.

$$\text{Heat} = (Q/R_S - f \cdot P/R_{V.B.}) \cdot f \cdot P \cdot S$$

where

Heat = Total heat added to can + sample, Joules

$R_S$ = Resistance of Standard Resistor, 1.00044 ohms

$R_{V.B.}$ = Resistance of Volt Box, 60000 ohms

f = Volt Box reduction ratio factor, 200

P = Voltage across volt box, absolute volts

P·f = Voltage across heater, absolute volts

Q = Voltage across standard resistor, absolute volts

S = Total time of heating interval, seconds.

The heat capacity of the calorimeter can plus sample is the heat input divided by the temperature rise during the time S. The temperature assigned to the heat capacity was the arithmetic average of the initial and final temperatures.

The heat capacity of the can had been determined by Hwa[21] from -117 to 32°C on the IPTS-48. Hwa fit the data to an equation of the form

$$(C_P)_{can} = (A_0 + A_1 \cdot t + A_2 \cdot t^2 + A_3 \cdot t^3 + A_1 \cdot t^4) \cdot 4.184 \quad .$$

The coefficients are given in Table 20.

Table 20. Heat Capacity of Calorimeter Can.

| Coefficient | Value |
|---|---|
| $A_0$ | 16.150851 |
| $A_1$ | 1.4611653(-2) |
| $A_2$ | - 9.8269990(-6) |
| $A_3$ | 1.1551778(-7) |
| $A_4$ | - 1.9636810(-9) |

Hwa's calibration of the can was used without recalibration because

1. The weight of the can was ± 20 milligrams of the weight when Hwa calibrated the can. This fluctuation was due to the variation

of the solder used to seal the caps. This variation has a negligible effect on the heat capacity (± 0.003 Joule/K).

2. Heat capacities of pure components agree with those of other laboratories which have reported precision measurements. The heat capacity of the can evaluated at the mean temperature was subtracted from the total heat capacity to yield the heat capacity of the sample. The heat capacity calculated on the IPTS-48 was converted to the IPTS-68 using the coefficients given in Table 5, Appendix A. The heat capacity of the sample was divided by the number of moles in the can to obtain the molar heat capacity of the sample which is given in Appendix B.

Sample Calculation of the Heat Capacity of the Pure Liquid

The data for a heat capacity measurement of n-heptane are given in Table 21. From the data in Table 21 and the weight of the sample,

Table 21. Calorimetric Data for Sample Calculation of Heat Capacity.

| | |
|---|---|
| Initial Resistance | N = 25.91865 ohms<br>R = 25.98455 ohms |
| Average Potentials | P = 0.0581452 volts<br>Q = 0.0785547 volts |
| Time of Heating Interval | S = 1238.34 seconds |
| Final Resistance | N = 26.33904 ohms<br>R = 26.40467 ohms |

104.380 gms., the following data were calculated

| | |
|---|---|
| Weight of sample in vacuo | 104.541 grams |
| Initial resistance of platinum thermometer | 25.561662 ohms |
| Initial temperature, IPTS 1948 | 273.7484 K |
| Initial temperature, IPTS 1968 | 273.7485 K |
| Heat input | 1127.954 Joules |
| Final resistance of platinum thermometer | 25.951600 ohms |
| Final temperature, IPTS 1948 | 277.5905 K |
| Final temperature, IPTS 1968 | 277.5889 K |
| Mean temperature, IPTS 1968 | 275.6687 K |
| Temperature increment | 3.8404 $\pm$ 0.001 K |

The heat capacity of the can at 275.6687 K was calculated to be 67.729 Joules/K using the polynomial given in Table 20. The heat capacity of n-heptane at 275.6687 K was

$$C_{P_h} = (1127.954/3.8404 - 67.729)\ (100.20557/104.541)$$
$$= 216.61 \text{ Joules/gm. mole-K.}$$

The heat capacity was not corrected for the heat of vaporization effect or the heat capacity of the gas phase above the liquid. The heat of vaporization effect was largest for ethanol. Near 308 K the effect was 0.06 Joules/gm. mole-K. This correction, which decreases rapidly with temperature, was not made. The vapor space above the liquid was approximately 10 milliliters. This vapor was composed of gaseous nitrogen and the vapor of the liquid sample. This effect of the heat capacity of the vapor was a maximum of about 0.01 Joules/K and was neglected.

## Sample Calculation of the Heat Capacity and Excess Heat Capacity of the Mixtures

The data for a heat capacity measurement of 2-propanol + n-heptane are given in Table 22. From the data in Table 22 and the weight of the

Table 22. Calorimetric Data for Sample Calculation of Heat Capacity for a Composition of 2-Propanol + n-Heptane of $x_a$ = 0.0809.

| | |
|---|---|
| Initial Resistance | N = 25.91672 ohms<br>R = 26.02070 ohms |
| Average Potentials | P = 0.0675397 volts<br>Q = 0.0912400 volts |
| Time of Heating Interval | S = 1223.80 seconds |
| Time of Heating Interval | N = 26.42040 ohms<br>R = 26.52722 ohms |

sample, 103.051 grams, the following data were calculated

| | |
|---|---|
| Weight of sample in vacuo | 103.210 grams |
| Initial resistance of platinum thermometer | 25.96871 ohms |
| Initial temperature, IPTS 1948 | 277.7592 K |
| Initial temperature, IPTS 1968 | 277.7575 K |
| Heat Input | 1503.904 Joules |
| Final resistance of platinum thermometer | 26.47381 ohms |
| Final temperature, IPTS 1948 | 282.7428 K |
| Final temperature, IPTS 1968 | 282.7390 K |
| Mean temperature, IPTS 1968 | 280.2482 K |
| Temperature increment | 4.9815 $\pm$ 0.001 K |

The heat capacity of the can at 280.2482 K was calculated to be 67.988 Joules/K using the polynomial given in Table 20. The total number of moles in the solution was

$$\text{Total moles} = (0.0501)\ (103.210)/(60.09661) + (0.9499)\ (103.210)/(100.20557)$$

$$= 1.0644 \text{ moles.}$$

The molar heat capacity of the solution at 280.2482 K was

$$C_P^S = (1503.904/4.9815 - 67.988)/1.0644$$

$$= 219.73 \text{ Joules/gm. mole-K.}$$

The heat capacities of 2-propanol and n-heptane at 280.2482 K were calculated to be 142.000 and 218.147 Joules/gm. mole-K respectively from the polynomials given in Table 12, Appendix B. The excess heat capacity by definition is

$$C_P^E = C_P^S - (x_a\ C_{pa} + x_h\ C_{p_h})$$

$$= 219.73 - (0.0809)(142.000) - (0.9191)(218.147)$$

$$= 7.75 \text{ Joules/gm. mole-K}$$

and was assigned the mean temperature 280.2482 K.

# APPENDIX E

## PURIFICATION AND CHARACTERIZATION OF MATERIALS

The sources of the chemicals employed are Phillips Petroleum Company, Fisher Scientific Company, and U.S. Industrial Chemicals for n-heptane, 2-propanol, and ethanol, respectively. The specifications of the vendors are for n-heptane: a minimum purity of 99 mole per cent; for 2-propanol: certified with a purity of 99 mole per cent; and for ethanol: reagent quality, 200 proof.

The ethanol was purified by a method described by Fieser.[12] A vacuum jacketed, strip-silvered distilling column packed with 1/8 inch diameter glass helices was employed in the purification. The specifications of the column are 60 inches in length with an I.D. of 0.5 inches. The distilling head was a vacuum type although the distillation was performed at atmospheric pressure under an atmosphere of dry air. The n-heptane was not purified but a distillation using the same still was made at a later date by Holzhauer[20], who showed calorimetrically that the purity was not improved significantly.

The 2-propanol, which was dried over calcium hydride in a dry box, was not purified further. The ethanol and 2-propanol were stored in a dry box after purification under an atmosphere of dry gaseous nitrogen.

The purity of the components was determined by a calorimetric technique described by Rossini[45]. The method involved partial freezing

of the sample, equilibrating the sample, and numerous heating periods until all the sample was melted. The melting point was also determined in this experiment.

The calorimeter can, which contains the sample, was cooled under a high vacuum in a bath of liquid nitrogen. Each of the pure samples exhibited supercooling before the freezing process started. The start of the freezing process was marked by an increase in temperature due to the evolution of heat of fusion. After a large part of the sample was frozen equilibrium was obtained. The melting process was carried out in the same manner as a heat capacity measurement. A quantity of heat was added to the sample and a new equilibrium temperature was reached. The equilibration took more than one hour whereas for a heat capacity measurement in the liquid region equilibrium was obtained in 10 minutes. The heating periods were repeated until all the sample was melted.

The fraction melted was calculated by taking the enthalpy at the melting point as zero. The enthalpy at each equilibrium temperature was calculated from the accumulated heat, the heat capacity of the liquid and solid, and the heat of fusion. The heat capacity of the solid for each pure substance was taken from the literature to correct for the small heat effect of raising the temperature of the solid in the premelting region. The heat capacity of the liquid was measured in this laboratory. The heat of fusion was taken from the literature. The calculation permitted the determination of the per cent melted at any equilibrium temperature. The method did not require that the sample be completely frozen before determining the purity or melting point.

The melting point and purity of each pure substance were determined calorimetrically. The assumptions that were made are the liquid is an ideal solution, the solid phase of the major constituent is pure, the system is in thermodynamic equilibrium, and $x_2$ is small. These are the assumptions of Rossini[45], who also derives the relationship

$$x_2 = A \cdot F \cdot (T^* - T_e) \tag{51}$$

$$A = H_f/R \cdot (T^*)^2 \tag{52}$$

where $x_2$ is the mole fraction impurity; F is the fraction melted; A is the cryoscopic constant; $T^*$ is the true melting point of the major constituent; $T_e$ is the equilibrium temperature; $H_f$ is the heat of fusion; and R is the gas constant. Equation (51) can be rearranged to the form

$$T_e = T^* - (X_2/A)(1/F) \ . \tag{53}$$

A plot of the equilibrium temperature vs. (1/F) is a straight line. The intercept of the line is the true melting point and the slope times the cryoscopic constant is the mole fraction impurity. In this work the true melting point was determined graphically using Equation (53), and the mole fraction of the impurity was calculated using Equation (51). The melting point and purity determinations are summarized in Table 23.

For ethanol the heat of fusion, 1200 cal./gm. mole, reported by Kelley[24] was used. The cryoscopic constant, 0.0239 was calculated from this heat of fusion and the melting point determined in the present work. The melting point of ethanol determined in this laboratory and in other laboratories is summarized in Table 24. The melting point

measured in the present work agrees with that of Hwa[21] well within experimental error. This indicates that the condition of the calorimeter has not changed significantly since Hwa used it. In view of the differences in temperature scales of the various authors and the stated uncertainties, the melting points agree quite well.

For 2-propanol the heat of fusion, 1293 cal./gm mole, reported by Andon et al.[1] was used. The cryoscopic constant was calculated from this heat of fusion and the melting point determined in the present work. The melting points of 2-propanol are summarized in Table 24. The melting point determined in this work, 185.232 ± 0.04 K, agrees within experimental error with the value of Andon, et al. of 185.20 K.

For n-heptane the heat of fusion, 3355 ± cal/gm. mole, reported by McCullough and Messerly[34] was used. Other reliable values in the literature are 3351 ± 3 cal./gm. mole given by Douglas et al.[10] and 3357 ± 4 cal./gm. mole reported by Stull[55]. The melting points of n-heptane are summarized in Table 24. The melting point determined in the present work are in complete agreement with those determined by the U.S. Bureau of Mines[34], U.S. National Bureau of Standards[10] and Stull[55].

The excellent agreement of the melting points determined in the present work with other laboratories also using the International Temperature Scale, indicates the consistency of the temperature scale used in this laboratory. The melting points reported in this work were not corrected for pressure effects when making comparisons with freezing points determined at atmospheric pressure or with triple

points. The magnitude of this effect was estimated to be less than 0.007 degrees.

Table 23. Purity and Melting Point Determinations*.

Ethanol

| Per Cent Melted 100 F | Equilibrium Temperature $T_e$, K | Melting Point Impurity, $x_2$ |
|---|---|---|
| 31.93 | 158.840 | 0.00115 |
| 41.07 | 158.944 | 0.00046 |
| 50.37 | 158.957 | 0.00041 |
| 64.67 | 158.963 | 0.00043 |
| 83.80 | 158.965 | 0.00052 |

Melting Point of Pure Ethanol 158.991 ± 0.03 K
Mole Fraction Impurity 0.0006 ± 0.0002

2-Propanol

| Per Cent Melted 100 F | Equilibrium Temperature $T_e$, K | Mole Fraction Impurity, $x_2$ |
|---|---|---|
| 2.26 | 180.916 | 0.00185 |
| 22.35 | 184.846 | 0.00164 |
| 43.95 | 185.044 | 0.00157 |
| 56.88 | 185.100 | 0.00143 |
| 86.10 | 185.133 | 0.00162 |

Melting Point of Pure 2-Propanol 185.232 ± 0.04 K
Mole Fraction Impurity 0.0016 ± 0.0003

n-Heptane

| Per Cent Melted 100 F | Equilibrium Temperature $T_e$, K | Mole Fraction Impurity, $x_2$ |
|---|---|---|
| 36.86 | 182.386 | 0.00329 |
| 60.82 | 182.477 | 0.00262 |
| 93.33 | 182.498 | 0.00303 |

Melting Point of Pure n-Heptane 182.562 ± 0.04 K
Mole Fraction Impurity 0.0030 ± 0.0008

* All temperatures in this table are on the International Practical Temperature Scale of 1948 + 273.15.

Table 24. Melting Point of Pure Constituents.

Ethanol

| Author | Reference | Temperature Scale | Melting Point, K |
|---|---|---|---|
| Present work | | IPKS-54 | 158.991 ± 0.03 |
| Hwa | 21 | IPKS-54 | 159.015 ± 0.05 |
| Kelley | 24 | Unknown | 158.5 |
| Nikolaev et al. | 36 | Unknown | 158.8 ± 0.1 |
| A.P.I. | 46 | IPKS-54 | 158.75 |

2-Propanol

| Author | Reference | Temperature Scale | Melting Point, K |
|---|---|---|---|
| Present work | | IPKS-54 | 185.232 ± 0.04 |
| Kelley | 25 | Unknown | 184.67 |
| Andon et al. | 1 | IPKS-54 | 185.20 |
| A.P.I. | 46 | IPKS-54 | 184.75 |

n-Heptane

| Author | Reference | Temperature Scale | Melting Point, K |
|---|---|---|---|
| Present work | | IPKS-54 | 182.562 ± 0.04 |
| U.S. Bureau of Mines | 34 | IPKS-54 | 182.55 ± 0.05 |
| U.S. National Bureau of Standards | 10 | IPTS-48 | 182.56 ± 0.01 |
| Stull | 55 | IPTS-48 | 182.54 |
| A.P.I. | 46 | IPKS-54 | 182.54 |

# APPENDIX F

## DRIFT RATE STUDIES

Two possible alternatives for the environment of the cryostat are that the temperature of the bath can be adjusted as the sample is heated or a constant temperature bath can be used for a specific temperature range. The temperature of the bath used by Hwa[21] was adjusted as the temperature of the calorimeter can be changed. However, McGee[33] and Liu[31] used constant temperature baths in their work. For this reason a drift rate study was initiated to determine the effect of the bath on the heat capacity measurements.

The maximum effect on the heat capacity measurement would be expected when the temperature is high and the temperature difference between the can (or shields) and cryostat are at a maximum, since the driving forces for heat transfer are a maximum under these conditions. The constant temperature baths used were a liquid nitrogen bath, a dry ice-ethanol bath, and an ice-water bath. Rough experiments showed that below the normal sublimation point of dry ice (approximately -78°C) a liquid nitrogen bath could be used with a negligible effect on the heat capacity.

The determination of a drift rate for a particular bath and calorimeter can temperature involved:

1) Keeping the temperature difference between the shield and the calorimeter can as near as possible to some specified value (the final

temperature difference, $t_{shield} - t_{can}$, is obtained by monitoring the three, three-junction constantan chromel-P thermocouples TD1, TD2, and TD3 (see Chapter II),

2) Keeping the temperature difference between the guard ring and the shield as near to zero as possible (thermocouple, TD4),

3) Measuring the temperature of the calorimeter can over a period of one to two hours (any noted temperature change is referred to as the drift rate in degrees/hour).

The results of the drift rate study are given in Tables 25, 26, and 27. In some of the measurements the shield and calorimeter can were held at a constant temperature difference other than zero. These experiments gave an indication of the effect of shield control on heat capacity measurements. The results of a zero temperature difference showed that only near the upper temperature range of a bath was the drift rate large enough to cause a noticeable effect. A heat capacity measurement usually involved a five degree rise in temperature in 40 minutes and was made with as close to a zero temperature difference between the shield and the calorimeter can as possible. From the results given in Tables 25, 26, and 27 it is shown that the maximum effect on the heat capacity was less than the accuracy of 0.2 per cent claimed. The water bath did not afford a significant improvement over the ice-water bath. A comparison with the variable temperature bath was not possible since Hwa did not make a similar study. The drift rate results for the water bath, however, give an indication of the drift rate to be expected with the variable temperature bath. It was concluded that the constant temperature baths could be used with a negligible effect on the heat capacity.

Table 25. Drift Rates For Dry Ice-Ethanol Bath.

| $t_{can}$, °C | $t_{shield} - t_{can}$, °C | Drift Rate, °C/hr. |
|---|---|---|
| 23.6 | 0.00 | -0.006 |
| 23.6 | 0.10 | 0.009 |
| 23.6 | 0.20 | 0.025 |

Table 26. Drift Rates For Ice-Water Bath.

| $t_{can}$, °C | $t_{shield} - t_{can}$, °C | Drift Rate, °C/hr. |
|---|---|---|
| 0.0 | 0.00 | 0.001 |
| 0.1 | 0.00 | $-0.000_6$ |
| 0.1 | 0.05 | 0.006 |
| 0.1 | 0.10 | 0.011 |
| 0.2 | 0.00 | $0.000_4$ |
| 0.2 | 0.05 | 0.004 |
| 0.2 | 0.10 | 0.010 |
| 1.3 | 0.00 | $0.000_1$ |
| 21.7 | 0.00 | -0.002 |
| 34.2 | 0.00 | -0.007 |

Table 27. Drift Rate For Water Bath, 21°C.

| $t_{can}$, °C | $t_{shield} - t_{can}$, °C | Drift Rate, °C/hr. |
|---|---|---|
| 32.1 | 0.00 | -0.004 |

## APPENDIX G

## EFFECT OF PRESSURE ON THE EXCESS THERMODYNAMIC PROPERTIES

The excess thermodynamic properties are assumed to be at constant pressure. The error in having made this assumption for measurement made at constant temperature and composition is determined from the thermodynamic relations

$$\left(\frac{\partial C_p^E}{\partial P}\right)_{T,x} = -T\left(\frac{\partial^2 V^E}{\partial T}\right)_{P,x} \tag{54}$$

$$\left(\frac{\partial H^E}{\partial P}\right)_{T,x} = V^E - T\left(\frac{\partial V^E}{\partial T}\right)_{P,x} \tag{55}$$

$$\left(\frac{\partial S^E}{\partial P}\right)_{T,x} = -\left(\frac{\partial V^E}{\partial T}\right)_{P,x} \tag{56}$$

$$\left(\frac{\partial G^E}{\partial P}\right)_{T,x} = V^E \quad . \tag{57}$$

Integrating Equations (54) to (57)

$$\Delta C_p^E = -\int_{P_1}^{P_2} T\left(\frac{\partial^2 V^E}{\partial T^2}\right)_{p,x} dP \tag{58}$$

$$\Delta H^E = \int_{P_1}^{P_2} \left[V^E - T\left(\frac{\partial V^E}{\partial T}\right)_{p,x}\right] dP \tag{59}$$

$$\Delta S^E = - \int_{P_1}^{P_2} \left(\frac{\partial V^E}{\partial T}\right)_{p,x} dP \qquad (60)$$

$$\Delta G^E = \int_{P_1}^{P_2} V^E \, dP \quad . \qquad (61)$$

All measurements in this work are made at less than one atmosphere, therefore the maximum error occurs when $P_1$ and $P_2$ are zero and one atmosphere, respectively. The excess volume or the first and second derivative of the excess volume with respect to temperature are not known as a function of pressure. Therefore, Equations (58) to (61) are integrated assuming these properties constant with respect to pressure.

Van Ness et al.[60] report the excess volume at 25 and 45°C for the ethanol + n-heptane system. The excess volume is a maximum of 0.465 cc/gm. mole at a mole fraction of ethanol of 0.5. At this mole fraction $\left(\frac{\partial V^E}{\partial T}\right)_{p,x}$ is estimated to be 0.0077 cc/gm. mole-K. For the 2-propanol + n-heptane system Van Ness et al.[59] report the excess volume at 25°C. The excess volume at a mole fraction of 2-propanol of 0.5 is 0.585 cc/gm. mole. Van Ness estimated $\left(\frac{\partial V^E}{\partial T}\right)_{p,x}$ to be 0.0075 cc/gm. mole-K at this mole fraction for 25°C.

The effect of pressure on the excess properties of the ethanol + n-heptane and 2-propanol + n-heptane systems is summarized in Table 28. The actual pressure in the system at the lowest temperature is estimated to be approximately 0.6 atmosphere, hence the error is even less. The effect of pressure on these properties are much less than the uncertainly of the data. Therefore, in all calculations the corrections are not made for this effect.

Table 28. Effect of Pressure on the Excess Thermodynamic Properties.

| Ethanol + n-Heptane | | |
|---|---|---|
| Property | Effect of Pressure | |
| $H^E$ | -0.186 | Joules/gm. mole |
| $S^E$ | -0.00078 | Joules/gm. mole-K |
| $G^E$ | 0.047 | Joules/gm. mole |

| 2-Propanol + n-Heptane | | |
|---|---|---|
| Property | Effect of Pressure | |
| $H^E$ | -0.167 | Joules/gm. mole |
| $S^E$ | -0.00076 | Joules/gm. mole-K |
| $G^E$ | 0.059 | Joules/gm. mole |

# APPENDIX H

## EMPIRICAL METHODS OF CORRELATING EXCESS GIBBS FREE ENERGY DATA

The historical methods for correlating excess Gibbs free energy data have used the Van Laar equation, Hildebrand solubility parameters, the Margules equation, the Wohl equation, and the Redlich-Kister equation. More recent methods are a modified form of the Redlich-Kister equation[35], the Wilson equation[64], the Renon equation[40], and the Wiehe-Bagley equation[62]. The Wilson equation has two parameters and the Renon equation has four parameters. Renon's equation, unlike Wilson's, is applicable to partially miscible as well as completely miscible systems. A modification of Wilson's equation[51] with three parameters is applicable to partially miscible systems. The Wiehe-Bagley equation, which has three parameters, is applicable to alcohol-inert solvent systems. Wiehe and Bagley[62] used -5900 cal./gm. mole for the parameter related to the breaking of a hydrogen bond, therefore, the equation is reduced to a two parameter relation.

It is desirable that any empirical method used to correlate excess Gibbs free energy data have as few adjustable parameters as possible. For this reason the Wilson equation and the Wiehe-Bagley equation are chosen for study and compared with the Redlich-Kister equation. This comparison was made for the ethanol + n-heptane and 2-propanol + n-heptane systems. An attempt was also made to correlate

the experimental excess enthalpy, excess entropy, and excess heat capacity data with the Redlich-Kister equation. These data could not be correlated over the complete temperature range of the data.

The Redlich-Kister equation of the form

$$G^E/x_a x_h \, R \cdot T = \sum_i Y_i (2 \cdot x_a - 1) \qquad (62)$$

and a modified Redlich-Kister equation of the form*

$$x_a x_R \, R \cdot T/G^E = \sum_i Z_i (2 \cdot x_a - 1) \qquad (63)$$

were used to fit the excess Gibbs free energy data of the ethanol + n-heptane and 2-propanol + n-heptane systems. A least square procedure using Forsyth orthogonal polynomials was employed in the fit.

The excess Gibbs free energy data of the ethanol + n-heptane system were fitted at 213.15, 243.15, 273.15, 283.15, and 303.15 K by Equation (62). The Redlich-Kister equation of the third degree gave an average deviation of 0.4 per cent at 213.15 K to 0.5 per cent at 303.15 K and a maximum deviation of 0.6 per cent. The constants of the Redlich-Kister equation are given in Table 29.

The excess Gibbs free energy data of the 2-propanol + n-heptane system were fitted at 183.15, 213.15, 243.15, 273.15, and 303.15 K by Equation (62). The Redlich-Kister equation of the third degree gave an average deviation of 0.1 per cent at 183.15 K to 0.5 per cent at 303.15 and a maximum deviation of 0.9 per cent. The constants of the Redlich-Kister equation are given in Table 29.

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* The function $x_a x_h/G^E$ versus $x_a$ presents a more nearly linear curve for polar systems than Equation (1).

Table 29. Coefficients, $Y_i$, of the Redlich-Kister Equation.

Ethanol + n-Heptane

| T,K | $Y_0$ | $Y_1$ | $Y_2$ | $Y_3$ |
|---|---|---|---|---|
| 213.15 | 2.51377152 | -0.14968385 | 0.78757798 | -0.21739949 |
| 243.15 | 2.44279941 | -0.17523976 | 0.71856915 | -0.23480745 |
| 273.15 | 2.37198776 | -0.18954058 | 0.65829521 | -0.21011523 |
| 283.15 | 2.34640695 | -0.18561736 | 0.63314865 | -0.20330324 |
| 303.15 | 2.28741179 | -0.17962956 | 0.57639737 | -0.15609169 |

2-Propanol + n-Heptane

| T,K | $Y_0$ | $Y_1$ | $Y_2$ | $Y_3$ |
|---|---|---|---|---|
| 183.15 | 2.34007886 | -0.14406708 | 0.68144265 | -0.58775074 |
| 213.15 | 2.26286353 | -0.15359015 | 0.62299344 | -0.61359251 |
| 243.15 | 2.19390953 | -0.14323938 | 0.57650083 | -0.61990438 |
| 273.15 | 2.11114823 | -0.11551626 | 0.52919683 | -0.60641919 |
| 303.15 | 1.99585136 | -0.09711133 | 0.47121389 | -0.50483579 |

The constants of the Redlich-Kister equation are only temperature dependent; therefore the constants were fitted to a function of temperature

$$Y_i = \sum_j y_{ij} T^j \qquad (64)$$

by a least square procedure. Combining Equations (64) and (62) leads to Equation (65) which fits the data as well as Equation (62). Equation (65) is a representation of the $G^E$ - T - x surface and is recommended for interpolation. The constants, $y_{ij}$, are

$$G^E/x_a x_h\, R\cdot T = \sum_i \sum_j (y_{iy}\, T)(2\cdot x_a - 1)^i \qquad (65)$$

given in Table 30.

Table 30. Coefficients, $y_{ij}$, of the Redlich-Kister Equation.

$$Y_i = \sum_j y_{ij}\, T^j$$

Ethanol + n-Heptane

| i/j | 0 | 1 | 2 | 3 |
|---|---|---|---|---|
| 0 | 4.30790462 | -1.83935423(-2)* | 6.60236393(-5) | -9.01678051(-8) |
| 1 | 5.49915259(-1) | -5.34587697(-3) | 9.69295632(-6) | 0 |
| 2 | 3.87875571 | -3.39501946(-2) | 1.27199241(-4) | -1.68707360(-7) |
| 3 | 9.63348881(-1) | -9.90740100(-3) | 2.04908589(-5) | 0 |

2-Propanol + n-Heptane

| i/j | 0 | 1 | 2 | 3 |
|---|---|---|---|---|
| 0 | 4.16884413 | -2.12760868(-2) | 8.47091810(-5) | -1.25916358(-7) |
| 1 | 1.32364171 | -1.80910649(-2) | 7.15343858(-5) | -9.00988580(-8) |
| 2 | 1.94595507 | -1.38963413(-2) | 5.09710183(-5) | -6.98627778(-8) |
| 3 | -2.36208315 | 2.68650274(-2) | -1.32576519(-4) | 2.11630586(-7) |

The excess Gibbs free energy data of the ethanol + n-heptane system were fitted at 213.15, 243.15, 273.15, 283.15, and 303.15 K by Equation (63). The "modified" Redlich-Kister equation of the second degree

gave an average deviation of 0.2 per cent at 213.15 K to 0.4 per cent at 303.15 K and a maximum deviation of 0.7 per cent. The constants of the modified Redlich-Kister are given in Table 31.

Table 31. Coefficients, $Z_i$, of the Modified Redlich-Kister Equation.

Ethanol + n-Heptane

| T,K | $Z_0$ | $Z_1$ | $Z_2$ |
|---|---|---|---|
| 213.15 | 0.39699623 | 0.02797073 | -0.10491155 |
| 243.15 | 0.40862211 | 0.03440657 | -0.10110556 |
| 273.15 | 0.42087757 | 0.03795718 | -0.09819076 |
| 283.15 | 0.42551149 | 0.03805584 | -0.09688390 |
| 303.15 | 0.43654203 | 0.03715437 | -0.09355230 |

2-Propanol + n-Heptane

| T,K | $Z_0$ | $Z_1$ | $Z_2$ | $Z_3$ |
|---|---|---|---|---|
| 183.15 | 0.42626831 | 0.03496783 | -0.09925297 | 0.04387724 |
| 213.15 | 0.44078144 | 0.03996262 | -0.09510430 | 0.04994907 |
| 243.15 | 0.45463321 | 0.04073157 | -0.09298121 | 0.05560978 |
| 273.15 | 0.47249531 | 0.03729221 | -0.09284702 | 0.06318343 |
| 303.15 | 0.49998091 | 0.03455878 | -0.09508854 | 0.06149811 |

The excess Gibbs free energy data of the 2-propanol + n-heptane system were fitted at 183.15, 213.15, 243.15, 273.15, and 303.15 K by Equation (63). The modified Redlich-Kister equation of

the third degree gave an average deviation of 0.4 per cent at 183.15 K to 0.2 per cent at 303.15 K and a maximum deviation of 0.8 per cent. The constants of the modified Redlich-Kister equation are given in Table 31.

Table 32. Coefficients, $z_{ij}$, of the Modified Redlich-Kister Equation.

$$Z_i = \sum_j z_{ij} T^j$$

Ethanol + n-Heptane

| i/j | 0 | 1 | 2 | 3 |
|---|---|---|---|---|
| 0 | 7.72214294(-2) | 3.40415957(-3) | -1.27523060(-5) | 1.79213755(-8) |
| 1 | -5.49945926(-3) | -2.58704138(-4) | 3.44938478(-6) | -7.03291773(-9) |
| 2 | -3.71996388(-1) | 3.03210397(-3) | -1.16016611(-5) | 1.52716515(-8) |

2-Propanol + n-Heptane

| i/j | 0 | 1 | 2 | 3 |
|---|---|---|---|---|
| 0 | 1.72081872(-2) | 4.97405630(-3) | -2.07778171(-5) | 3.17433951(-8) |
| 1 | -2.56623349(-1) | 3.40053473(-3) | -1.26640266(-5) | 1.52215123(-8) |
| 2 | -1.56094822(-1) | 4.16947806(-4) | -3.83886287(-7) | -1.08064815(-9) |
| 3 | 3.25906432(-1) | -4.07343837(-3) | 1.88404782(-5) | -2.73081790(-8) |

As in the case of the Redlich-Kister equation, the constants of the modified Redlich-Kister equation are only temperature dependent;

therefore the constants were fitted to a function of temperature

$$Z_i = \sum_j z_{ij} T^j \qquad (66)$$

by a least square procedure. Combining Equations (66) and (63) leads to Equation (67), which fits the data as well as Equation (63). Equation (67) is a representation of the G-T-x surface and is recommended for interpolation. The constants, $z_{ij}$, are given

$$x_a x_h \, R \cdot T / G^E = \sum_i \sum_j (z_{ij} T^j) \, (2 \cdot x_a - 1)^i \qquad (67)$$

in Table 32.

In comparing the fits of the Redlich-Kister equation to the fits of the modified Redlich-Kister equation, the modified Redlich-Kister equation gave a slightly better fit to the derived excess Gibbs free energy data for the two binary systems studied in the present work with the same or fewer parameters.

The Wilson equation of the form[62]

$$G^E / R \cdot T = -x_a \mathrm{Ln}(x_a + D \cdot x_h) - x_h \, \mathrm{Ln}(x_h + C \cdot x_a) \qquad (68)$$

was used to fit the excess Gibbs free energy data of the ethanol + n-heptane and 2-propanol + n-heptane systems. A computer program was written to fit the Wilson equation to excess Gibbs free energy data. The program determines values of D and C for each isothermal set of experimental points. The arithmetic average of all the D's and C's at an isotherm gave an initial D and an initial C. A least square procedure

minimizing the sum of the squares of the residuals gave two equations to be solved iteratively for the "best" set of parameters. The iterative method employed was the Newton-Raphson method[53]. The initial iterates were the initial D and C found by the averaging procedure mentioned above. The iteration was stopped when the sum of the squares of the residuals was a minimum. The resultant D and C are the parameters of the Wilson equation which best fit the derived excess Gibbs free energy in a least square sense.

The excess Gibbs free energy data of the ethanol + n-heptane system were fitted at 213.15, 243.15, 273.15, and 303.15 K by Equation (68). The Wilson equation gave an average deviation of 0.4 per cent at 213.15 and 303.15 K and of 0.3 per cent at 243.15 and 273.15 K. The maximum deviation was 0.8 per cent. The constants of the Wilson equation are given in Table 33.

The excess Gibbs free energy data of the 2-propanol + n-heptane system were fitted at 183.15, 213.15, 243.15, 273.15, and 303.15 K by Equation (68). The Wilson equation gave an average deviation of 0.5 per cent at 183.15 K to 2.0 per cent at 303.15 K. The maximum deviation was 2.7 per cent. The constants of the Wilson equation are given in Table 33.

The Wilson equation fits the excess Gibbs free energy data about as well as the two forms of the Redlich-Kister equation. The important point is that the Wilson equation employs fewer parameters in representing the data.

Table 33. Coefficients of the Wilson Equation.

Ethanol + n-Heptane

| T,K | D | C |
|---|---|---|
| *303.15 | 0.06461 | 0.18921 |
| 273.15 | 0.04203 | 0.16394 |
| 243.15 | 0.03065 | 0.13578 |
| 213.15 | 0.02405 | 0.10243 |

2-Propanol + n-Heptane

| T,K | D | C |
|---|---|---|
| **303.15 | 0.08847 | 0.34426 |
| 273.15 | 0.05773 | 0.30733 |
| 243.15 | 0.04122 | 0.27456 |
| 213.15 | 0.03200 | 0.24154 |
| 183.15 | 0.02623 | 0.19946 |

* Using $G^E$ data of Van Ness, et al.,[60] at 303.15 K over the complete composition range gave D = 0.04405, C = 0.21669.

** Using $G^E$ data of Van Ness, et al.,[59] at 303.15 K over the complete composition range gave D = 0.05467, C = 0.40169.

The Wiehe-Bagley[62] equation of the form

$$G^E/R\cdot T = x_a \cdot \mathrm{Ln}(f) + x_h \mathrm{Ln}(\rho/b) + (1/KA) \cdot (x_a \mathrm{Ln}(1+KA) - b \mathrm{Ln}(f)) \quad (69)$$

where

$$f = \frac{\rho\cdot x_h + (1 + KA)\cdot x_a}{\rho\cdot x_h + x_a}$$

$$b = \rho\cdot x_h + x_a$$

$$KA = \mathrm{EXP}(SA + 1 - HA/R\cdot T) \quad (70)$$

was used to fit the excess Gibbs free energy data of the ethanol + n-heptane and 2-propanol + n-heptane systems. The Wiehe-Bagley equation is rigorously derivable from a quasichemical theory using the Flory-Huggins athermal model. Wiehe and Bagley[62] analyzed a number of alcohol-hydrocarbon systems at various isotherms near room temperature. The parameter HA is related to the enthalpy of hydrogen bonding. They selected a mean value, -5900 cal./gm. mole, given by Coulson[8]. This value was taken by them to be independent of the alcohol-hydrocarbon system or of temperature. The parameter SA is related to entropy of hydrogen bonding divided by R, the gas law constant. For the alcohol-hydrocarbon systems they studied, the value of SA was taken as -4.94 for the ethanol system and as -5.93 for the 2-propanol system. Once the temperature is specified KA is calculated from Equation (70). The parameter $\rho$ is treated as an adjustable parameter to fit either the

vapor-liquid equilibrium data or excess Gibbs free energy data as a function of composition at an isotherm.

In the present work a computer program was written to fit the excess Gibbs free energy data for the ethanol + n-heptane and 2-propanol + n-heptane systems (Tables 16 and 17). The above mentioned parameters HA and SA given by Wiehe and Bagley for ethanol[62] and 2-propanol[63], were used. Equation (70) was used to calculate KA at a temperature. Equation (69) was fitted to the excess Gibbs free energy data at an isotherm by determining $\rho$ for the two systems in a least square procedure in which Newton's method[53] was employed. The resultant $\rho$ is the parameter which best fits the excess Gibbs free energy data to the Wiehe-Bagley equation in a least square sense.

The excess Gibbs free energy data, Table 17, of the ethanol + n-heptane system were fitted at 213.15, 243.15, 273.15, and 303.15 K by Equation (69). The Wiehe-Bagley equation gave an average deviation of 0.6 per cent at 303.15 K to 1.8 per cent at 213.15. The constants of the Wiehe-Bagley equation are given in Table 34. The maximum deviation was 5.7 per cent at 213.15 K and 0.1023 mole fraction ethanol.

The excess Gibbs free energy data, Table 16, of the 2-propanol + n-heptane system were fitted at 183.15, 213.15, 243.15, 273.15, and 303.15 K by Equation (69). The constants of the Wiehe-Bagley equation are given in Table 34. The Wiehe-Bagley equation gave an average deviation of 3.0 per cent and a maximum deviation of 7.6 per cent at 183.15 K and 0.0809 mole fraction 2-propanol.

The correlation of the excess Gibbs free energy with the Wiehe-

Table 34. Coefficients of the Wiehe-Bagley Equation

Ethanol + n-Heptane

| T,K | HA Joules/gm. mole | SA | KA | ρ | dρ/dT |
|---|---|---|---|---|---|
| *303.15 | -24685.6 | -4.94 | 348.62 | 5.709 | 0.00216 |
| 273.15 | -24685.6 | -4.94 | 1022.14 | 5.743 | -0.00800 |
| 243.15 | -24685.6 | -4.94 | 3907.92 | 6.304 | -0.02976 |
| 213.15 | -24685.6 | -4.94 | 21793.69 | 8.402 | -0.11313 |

2-Propanol + n-Heptane

| T,K | HA Joules/gm. mole | SA | KA | ρ | dρ/dT |
|---|---|---|---|---|---|
| **303.15 | -24685.6 | -5.93 | 129.54 | 3.187 | -0.00010 |
| 273.15 | -24685.6 | -5.93 | 379.80 | 3.203 | -0.00149 |
| 243.15 | -24685.6 | -5.93 | 1452.09 | 3.299 | -0.01065 |
| 213.15 | -24685.6 | -5.93 | 8098.03 | 3.858 | -0.02250 |
| 183.15 | -24685.6 | -5.93 | 79301.29 | 4.625 | -0.02950 |

* Using $G^E$ data of Van Ness, et al.[60], at 303.15 K over the complete composition range gave all parameters the same except, ρ = 5.703.

** Using $G^E$ data of Van Ness, et al.[59], at 303.15 K over the complete composition range gave all parameters the same except, ρ = 3.193.

Table 35. Comparison of $G^E$ Calculated From Empirical Equations With $G^E$ Derived From $C_P^E$ For Ethanol + n-Heptane*

| T,K | $x_a$ | $G^E$ Derived | $G^E$ R-K | $G^E$ M-R-K | $G^E$ Wilson | $G^E$ W-B |
|---|---|---|---|---|---|---|
| 303.15 | 0.1023 | 669 | 665 | 666 | 668 | 679 |
| | 0.2805 | 1259 | 1267 | 1265 | 1258 | 1259 |
| | 0.4388 | 1448 | 1439 | 1441 | 1445 | 1443 |
| | 0.6140 | 1353 | 1359 | 1357 | 1363 | 1364 |
| | 0.8107 | 915 | 913 | 913 | 909 | 914 |
| 273.15 | 0.1023 | 639 | 635 | 635 | 639 | 665 |
| | 0.2805 | 1184 | 1192 | 1190 | 1181 | 1195 |
| | 0.4388 | 1354 | 1345 | 1348 | 1351 | 1355 |
| | 0.6140 | 1265 | 1270 | 1268 | 1275 | 1271 |
| | 0.8107 | 858 | 857 | 857 | 855 | 847 |
| 243.15 | 0.1023 | 589 | 586 | 585 | 590 | 620 |
| | 0.2805 | 1086 | 1093 | 1091 | 1082 | 1098 |
| | 0.4388 | 1240 | 1232 | 1236 | 1238 | 1241 |
| | 0.6140 | 1163 | 1168 | 1165 | 1172 | 1164 |
| | 0.8107 | 794 | 793 | 794 | 794 | 778 |
| 213.15 | 0.1023 | 530 | 527 | 528 | 532 | 560 |
| | 0.2805 | 978 | 983 | 981 | 972 | 990 |
| | 0.4388 | 1116 | 1110 | 1113 | 1115 | 1123 |
| | 0.6140 | 1054 | 1058 | 1056 | 1062 | 1061 |
| | 0.8107 | 728 | 727 | 727 | 730 | 720 |

* Units of $G^E$ are Joules/gm. mole.

Table 36. Comparison of $G^E$ Calculated From Empirical Equations With $G^E$ Derived From $C_p^E$ For 2-Propanol + n-Heptane*

| T,K | $x_a$ | $G^E$ Derived | $G^E$ R-K | $G^E$ M-R-K | $G^E$ Wilson | $G^E$ W-B |
|---|---|---|---|---|---|---|
| 303.15 | 0.0809 | 511 | 507 | 509 | 497 | 515 |
| | 0.2492 | 1044 | 1050 | 1046 | 1062 | 1074 |
| | 0.4219 | 1251 | 1244 | 1249 | 1268 | 1279 |
| | 0.5993 | 1201 | 1205 | 1202 | 1191 | 1204 |
| | 0.7984 | 812 | 811 | 812 | 785 | 800 |
| 273.15 | 0.0809 | 500 | 496 | 498 | 490 | 524 |
| | 0.2492 | 1004 | 1011 | 1006 | 1019 | 1044 |
| | 0.4219 | 1195 | 1188 | 1193 | 1208 | 1223 |
| | 0.5993 | 1143 | 1148 | 1144 | 1133 | 1140 |
| | 0.7984 | 770 | 768 | 769 | 751 | 751 |
| 243.15 | 0.0809 | 467 | 464 | 466 | 461 | 500 |
| | 0.2492 | 936 | 941 | 937 | 944 | 970 |
| | 0.4219 | 1107 | 1101 | 1106 | 1116 | 1127 |
| | 0.5993 | 1056 | 1060 | 1057 | 1050 | 1046 |
| | 0.7984 | 711 | 710 | 711 | 699 | 688 |
| 213.15 | 0.0809 | 423 | 420 | 424 | 419 | 456 |
| | 0.2492 | 850 | 853 | 849 | 852 | 881 |
| | 0.4219 | 1000 | 996 | 1000 | 1008 | 1025 |
| | 0.5993 | 956 | 958 | 956 | 952 | 958 |
| | 0.7984 | 646 | 645 | 646 | 640 | 637 |
| 183.15 | 0.0809 | 373 | 372 | 376 | 371 | 401 |
| | 0.2492 | 756 | 757 | 753 | 753 | 775 |
| | 0.4219 | 885 | 884 | 888 | 895 | 907 |
| | 0.5993 | 854 | 853 | 851 | 850 | 854 |
| | 0.7984 | 582 | 581 | 582 | 579 | 575 |

* Units of $G^E$ are Joules/gm. mole.

Bagley equation was a theoretical approach in which only the major effect of chemical interaction was considered. Therefore it was to be expected that as good a fit would not necessarily be obtained in this case as with the empirical equations. The excess Gibbs free energy calculated from each empirical or semi-empirical equation is compared to the derived excess Gibbs free data in Tables 35 and 36.

The activity coefficients were derived from the excess Gibbs free energy using Equations (9) and (10) of Chapter IV. The excess Gibbs free energy is specified by Equations (62), (68), or (69) together with the respective parameters given in Tables 29, 33, or 34. Explicit relations for the activity coefficients have been taken from the literature[63]. The activity coefficients calculated from the Redlich-Kister equation, Wilson equation, and Wiehe-Bagley equation are given in Tables 37 and 38.

Table 37. Activity Coefficients of Ethanol + n-Heptane

T = 303.15 K

| | R-K* | | W** | | W-B*** | |
|---|---|---|---|---|---|---|
| $x_a$ | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ |
| 0.0 | 3.200 | 0 | 3.550 | 0 | 3.956 | 0 |
| 0.1 | 2.106 | 0.054 | 1.291 | 0.064 | 2.005 | 0.072 |
| 0.2 | 1.421 | 0.172 | 0.994 | 0.171 | 1.387 | 0.177 |
| 0.3 | 0.996 | 0.312 | 0.757 | 0.298 | 1.011 | 0.301 |
| 0.4 | 0.722 | 0.458 | 0.567 | 0.445 | 0.742 | 0.446 |
| 0.5 | 0.527 | 0.617 | 0.411 | 0.618 | 0.533 | 0.616 |
| 0.6 | 0.370 | 0.809 | 0.280 | 0.826 | 0.366 | 0.821 |
| 0.7 | 0.233 | 1.065 | 0.171 | 1.082 | 0.229 | 1.076 |
| 0.8 | 0.116 | 1.418 | 0.084 | 1.413 | 0.119 | 1.409 |
| 0.9 | 0.032 | 1.899 | 0.021 | 1.874 | 0.037 | 1.880 |
| 1.0 | 0 | 2.528 | 0 | 2.600 | 0 | 2.646 |

T = 273.15 K

| | R-K* | | W** | | W-B*** | |
|---|---|---|---|---|---|---|
| $x_a$ | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ |
| 0.0 | 3.430 | 0 | 4.005 | 0 | 5.015 | 0 |
| 0.1 | 2.206 | 0.060 | 1.546 | 0.075 | 2.086 | 0.088 |
| 0.2 | 1.463 | 0.188 | 1.153 | 0.186 | 1.423 | 0.201 |
| 0.3 | 1.017 | 0.334 | 0.868 | 0.316 | 1.032 | 0.330 |
| 0.4 | 0.740 | 0.482 | 0.648 | 0.466 | 0.754 | 0.479 |
| 0.5 | 0.546 | 0.640 | 0.471 | 0.642 | 0.541 | 0.653 |
| 0.6 | 0.387 | 0.835 | 0.324 | 0.853 | 0.371 | 0.861 |
| 0.7 | 0.245 | 1.101 | 0.203 | 1.115 | 0.232 | 1.120 |
| 0.8 | 0.122 | 1.472 | 0.103 | 1.460 | 0.120 | 1.457 |
| 0.9 | 0.034 | 1.978 | 0.030 | 1.950 | 0.037 | 1.934 |
| 1.0 | 0 | 2.631 | 0 | 2.766 | 0 | 2.709 |

* Calculated from the Redlich-Kister equation.
** Calculated from the Wilson equation.
*** Calculated from the Wiehe-Bagley equation.

(Continued)

Table 37. Activity Coefficients of Ethanol + n-Heptane (Continued)

T = 243.15 K

| | R-K* | | W** | | W-B*** | |
|---|---|---|---|---|---|---|
| $x_a$ | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ |
| 0.0 | 3.571 | 0 | 4.349 | 0 | 6.273 | 0 |
| 0.1 | 2.274 | 0.064 | 1.709 | 0.081 | 2.133 | 0.098 |
| 0.2 | 1.498 | 0.197 | 1.253 | 0.195 | 1.451 | 0.214 |
| 0.3 | 1.041 | 0.347 | 0.940 | 0.327 | 1.052 | 0.346 |
| 0.4 | 0.762 | 0.496 | 0.703 | 0.478 | 0.771 | 0.496 |
| 0.5 | 0.567 | 0.655 | 0.514 | 0.656 | 0.555 | 0.673 |
| 0.6 | 0.406 | 0.852 | 0.358 | 0.870 | 0.382 | 0.884 |
| 0.7 | 0.259 | 1.127 | 0.228 | 1.139 | 0.241 | 1.148 |
| 0.8 | 0.130 | 1.518 | 0.120 | 1.497 | 0.126 | 1.494 |
| 0.9 | 0.036 | 2.055 | 0.037 | 2.024 | 0.040 | 1.991 |
| 1.0 | 0 | 2.751 | 0 | 2.966 | 0 | 2.828 |

T = 213.15 K

| | R-K* | | W** | | W-B*** | |
|---|---|---|---|---|---|---|
| $x_a$ | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ |
| 0.0 | 3.668 | 0 | 4.625 | 0 | 7.742 | 0 |
| 0.1 | 2.336 | 0.065 | 1.827 | 0.086 | 2.182 | 0.103 |
| 0.2 | 1.537 | 0.202 | 1.330 | 0.201 | 1.492 | 0.220 |
| 0.3 | 1.070 | 0.356 | 0.998 | 0.333 | 1.090 | 0.353 |
| 0.4 | 0.786 | 0.507 | 0.750 | 0.485 | 0.806 | 0.505 |
| 0.5 | 0.591 | 0.666 | 0.553 | 0.665 | 0.587 | 0.684 |
| 0.6 | 0.429 | 0.865 | 0.390 | 0.883 | 0.410 | 0.900 |
| 0.7 | 0.278 | 1.147 | 0.254 | 1.159 | 0.263 | 1.173 |
| 0.8 | 0.142 | 1.559 | 0.139 | 1.533 | 0.142 | 1.539 |
| 0.9 | 0.040 | 2.145 | 0.047 | 2.105 | 0.048 | 2.088 |
| 1.0 | 0 | 2.934 | 0 | 3.255 | 0 | 3.125 |

Table 38. Activity Coefficients of 2-Propanol + n-Heptane.

T = 303.15 K

| $x_a$ | Van Ness, et al.* | | R-K** | | W*** | | W-B**** | |
|---|---|---|---|---|---|---|---|---|
| | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ |
| 0.0 | 3.440 | 0 | 3.069 | 0 | 3.081 | 0 | 3.436 | 0 |
| 0.1 | 1.749 | 0.068 | 1.838 | 0.059 | 0.942 | 0.055 | 1.825 | 0.063 |
| 0.2 | 1.200 | 0.162 | 1.184 | 0.171 | 0.728 | 0.154 | 1.245 | 0.163 |
| 0.3 | 0.870 | 0.270 | 0.839 | 0.283 | 0.545 | 0.274 | 0.888 | 0.280 |
| 0.4 | 0.635 | 0.397 | 0.634 | 0.393 | 0.395 | 0.413 | 0.634 | 0.416 |
| 0.5 | 0.449 | 0.548 | 0.474 | 0.523 | 0.271 | 0.572 | 0.441 | 0.574 |
| 0.6 | 0.301 | 0.729 | 0.324 | 0.708 | 0.171 | 0.757 | 0.290 | 0.758 |
| 0.7 | 0.184 | 0.947 | 0.184 | 0.969 | 0.092 | 0.975 | 0.172 | 0.978 |
| 0.8 | 0.094 | 1.219 | 0.075 | 1.299 | 0.035 | 1.236 | 0.082 | 1.247 |
| 0.9 | 0.026 | 1.606 | 0.014 | 1.639 | 0.002 | 1.560 | 0.023 | 1.587 |
| 1.0 | 0 | 2.123 | 0 | 1.865 | 0 | 1.978 | 0 | 2.039 |

* From experimental data of Van Ness, et al.[59]
** Calculated from the Redlich-Kister equation.
*** Calculated from the Wilson equation.
**** Calculated from the Wiehe-Bagley equation.

T = 273.15 K

| $x_a$ | R-K** | | W*** | | W-B**** | |
|---|---|---|---|---|---|---|
| | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ |
| 0.0 | 3.362 | 0 | 3.545 | 0 | 4.482 | 0 |
| 0.1 | 1.966 | 0.067 | 1.245 | 0.067 | 1.937 | 0.083 |
| 0.2 | 1.241 | 0.190 | 0.929 | 0.174 | 1.294 | 0.192 |
| 0.3 | 0.874 | 0.310 | 0.687 | 0.298 | 0.915 | 0.317 |
| 0.4 | 0.663 | 0.422 | 0.498 | 0.441 | 0.650 | 0.459 |
| 0.5 | 0.499 | 0.557 | 0.347 | 0.606 | 0.451 | 0.621 |
| 0.6 | 0.341 | 0.751 | 0.226 | 0.797 | 0.296 | 0.811 |
| 0.7 | 0.192 | 1.029 | 0.129 | 1.025 | 0.175 | 1.035 |
| 0.8 | 0.075 | 1.380 | 0.057 | 1.302 | 0.084 | 1.309 |
| 0.9 | 0.013 | 1.728 | 0.011 | 1.654 | 0.023 | 1.655 |
| 1.0 | 0 | 1.918 | 0 | 2.122 | 0 | 2.144 |

(Continued)

Table 38. Activity Coefficients of 2-Propanol + n-Heptane. (Continued)

T = 243.15 K

| | R-K** | | W*** | | W-B**** | |
|---|---|---|---|---|---|---|
| $x_a$ | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ |
| 0.0 | 3.534 | 0 | 3.914 | 0 | 5.790 | 0 |
| 0.1 | 2.060 | 0.071 | 1.450 | 0.075 | 1.991 | 0.096 |
| 0.2 | 1.292 | 0.201 | 1.058 | 0.185 | 1.320 | 0.210 |
| 0.3 | 0.903 | 0.328 | 0.779 | 0.313 | 0.932 | 0.338 |
| 0.4 | 0.681 | 0.446 | 0.566 | 0.459 | 0.662 | 0.482 |
| 0.5 | 0.513 | 0.584 | 0.398 | 0.626 | 0.459 | 0.648 |
| 0.6 | 0.352 | 0.782 | 0.263 | 0.823 | 0.302 | 0.840 |
| 0.7 | 0.200 | 1.067 | 0.154 | 1.059 | 0.179 | 1.069 |
| 0.8 | 0.080 | 1.427 | 0.072 | 1.351 | 0.086 | 1.348 |
| 0.9 | 0.014 | 1.793 | 0.017 | 1.729 | 0.024 | 1.703 |
| 1.0 | 0 | 2.007 | 0 | 2.251 | 0 | 2.177 |

T = 213.15 K

| | R-K** | | W*** | | W-B**** | |
|---|---|---|---|---|---|---|
| $x_a$ | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ |
| 0.0 | 3.653 | 0 | 4.200 | 0 | 7.391 | 0 |
| 0.1 | 2.133 | 0.073 | 1.591 | 0.080 | 2.047 | 0.102 |
| 0.2 | 1.335 | 0.209 | 1.148 | 0.193 | 1.364 | 0.218 |
| 0.3 | 0.929 | 0.341 | 0.844 | 0.322 | 0.970 | 0.348 |
| 0.4 | 0.699 | 0.463 | 0.616 | 0.470 | 0.695 | 0.495 |
| 0.5 | 0.527 | 0.604 | 0.436 | 0.640 | 0.487 | 0.665 |
| 0.6 | 0.365 | 0.804 | 0.292 | 0.842 | 0.324 | 0.864 |
| 0.7 | 0.210 | 1.094 | 0.175 | 1.086 | 0.195 | 1.104 |
| 0.8 | 0.086 | 1.466 | 0.084 | 1.393 | 0.096 | 1.403 |
| 0.9 | 0.016 | 1.856 | 0.022 | 1.801 | 0.028 | 1.795 |
| 1.0 | 0 | 2.119 | 0 | 2.389 | 0 | 2.346 |

(Continued)

Table 38. Activity Coefficients of 2-Propanol + n-Heptane. (Continued)

T = 183.15 K

| | R-K** | | W*** | | W-B**** | |
|---|---|---|---|---|---|---|
| $x_a$ | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ | Ln $\gamma_a$ | Ln $\gamma_h$ |
| 0.0 | 3.753 | 0 | 4.441 | 0 | 9.533 | 0 |
| 0.1 | 2.203 | 0.074 | 1.705 | 0.084 | 2.091 | 0.105 |
| 0.2 | 1.383 | 0.214 | 1.225 | 0.198 | 1.404 | 0.221 |
| 0.3 | 0.961 | 0.351 | 0.903 | 0.329 | 1.006 | 0.352 |
| 0.4 | 0.724 | 0.478 | 0.664 | 0.478 | 0.727 | 0.502 |
| 0.5 | 0.549 | 0.621 | 0.475 | 0.652 | 0.515 | 0.675 |
| 0.6 | 0.384 | 0.823 | 0.323 | 0.859 | 0.347 | 0.880 |
| 0.7 | 0.226 | 1.118 | 0.198 | 1.113 | 0.213 | 1.130 |
| 0.8 | 0.097 | 1.508 | 0.099 | 1.441 | 0.107 | 1.449 |
| 0.9 | 0.020 | 1.941 | 0.028 | 1.891 | 0.032 | 1.882 |
| 1.0 | 0 | 2.290 | 0 | 2.586 | 0 | 2.531 |

# APPENDIX I

## CORRELATION OF THE DERIVED EXCESS THERMODYNAMIC PROPERTIES WITH THE THEORY OF ASSOCIATED SOLUTIONS

### Volume Fraction Model

The parameters K, $H^{o}$, $\beta$, and $\beta'$ had to be determined in order to calculate the excess thermodynamic properties. The "best" sets of $\beta$ and $\beta'$ parameters were found by a least squares technique and sets of K and $H^{o}$ parameters as given below.

The parameter K is related to the chemical interactions in the form of hydrogen bonds. The volume fraction model considered here separates the interactions into chemical and physical types. The parameter K has been determined at 50°C by Renon and Prausnitz[44] to be 150 for ethanol-hydrocarbon systems and 60 for 2-propanol-hydrocarbon systems. They determined these values of K by considering the totality of excess property data available for each alcohol-hydrocarbon mixture from 0 to 65°C. In this determination they gave more weight to the excess enthalpy data at lower temperatures and higher alcohol mole fractions. They have also suggested a value of -7500 cal./gm. mole (-31380 Joules/mole) be used for $H^{o}$ based on the totality of the excess property data.

Having specified K at 50°C and $H^{o}$ then the van't Hoff relation

$$\frac{d \ln K}{D T} = \frac{H^{o}}{R T^{2}} \qquad (71)$$

was used to calculate K at other temperatures. The parameters $\beta$ and $\beta'$ were then determined as follows

1) Values of $\beta$ were chosen by trial and error until the sum of the squares at an isotherm

$$\Sigma (G^E_{calc} - G^E_{der})^2 \qquad (72)$$

was a minimum. The initial iterate was always $\beta$ equal to zero and the domain of $\beta$ search was from 0 to 30. The iteration was such that the sum of the squares ($\Sigma^2$) near the minimum was insensitive to the choice of $\beta$. As $\beta$ varied from the least square value the $\Sigma^2$ increased rapidly. For example, for the $G^E$ data of ethanol + n-heptane at 303.15 K the minimum of the sum of the squares ($\Sigma^2$) was 3.86(03)* at a $\beta$ of 9.78. Varying $\beta$ to 9.9 gave a $\Sigma^2$ of 3.88(03), $\beta$ to 8.88 gave a $\Sigma^2$ of 5.24(03), and $\beta$ to 6 gave a $\Sigma^2$ of 24.351(03). The excess Gibbs free energy, $G^E_{calc}$, is calculated from Equation (24) in Chapter V. The excess Gibbs free energy, $G^E_{der}$, is taken from Table 16 or 17, Appendix C.

2) Values of $\beta'$ were chosen by trial and error until the sum of the squares at an isotherm

$$\Sigma (H^E_{calc} - H^E_{der})^2 \qquad (73)$$

was a minimum. The initial iterate was always $\beta'$ equal to zero and the domain of $\beta'$ searched was from 0 to 30. Like the iteration for $\beta$, the iteration for $\beta'$ was such that the sum of the squares ($\Sigma^2$) near

* The numbers in parenthesis indicate multiplication by 10 raised to this power.

the minimum was insensitive to the choice of $\beta'$. Also as $\beta'$ varied from the least square value the $\Sigma^2$ increased rapidly. For example, for the $H^E$ data of ethanol + n-heptane at 303.15 K the minimum of the sum of the squares ($\Sigma^2$) was 2.07(03) at a $\beta'$ of 7.58. Varying $\beta'$ to 7.48 gave a $\Sigma^2$ of 2.10(03), $\beta'$ to 6.58 gave a $\Sigma^2$ of 3.66(03), and $\beta'$ to 4 gave a $\Sigma^2$ of 20.99(03). The excess enthalpy, $H^E_{calc}$, was calculated from Equation (35) in Chapter V. The excess enthalpy, $H^E_{der}$, is taken from Table 16 or 17, Appendix C.

The set of parameters were determined 1) for the 2-propanol + n-heptane system at 303.15, 273.15, 243.15, 213.15, and 183.15 K, 2) for the ethanol + n-heptane system at 303.15, 273.15, 243.15, and 213.15 K, and 3) for the ethanol + methylcyclohexane system at 303.15, 273.15, 243.15, and 213.15 K. The derived excess thermodynamic properties for the ethanol + methylcyclohexane system are given by Hwa[22]. The sets of parameters are given in Table 39.

In an attempt to find an improved correlation of the excess property data, three variations of the volume fraction model were studied. These variations included 1) varying $H^o$ but keeping it temperature independent, 2) varying the equilibrium constant at 50°C, and 3) making $H^o$ temperature dependent

$$H^o = H^o(323.15) + A(T - 323.15) \quad .$$

The variations will now be discussed in light of the ethanol + n-heptane system at 303.15 K. The first variation ($H^o$ at 323.15 from -31380 to -26380 Joules/mole) resulted in a slightly improved

Table 39. Parameters of the Volume Fraction Associated Theory Model.

2-Propanol + n-Heptane

| T,K | $H^{\circ}$ Joules/gm. mole | K | β Joules/cc | β' Joules/cc |
|---|---|---|---|---|
| 303.15 | -31380 | 130 | 6.28 | 7.58 |
| 273.15 | -31380 | 509 | 6.56 | 5.68 |
| 243.15 | -31380 | 2799 | 6.76 | 6.22 |
| 213.15 | -31380 | 24878 | 7.06 | 7.70 |
| 183.15 | -31380 | 452308 | 7.64 | 9.61 |

Ethanol + n-Heptane

| T,K | $H^{\circ}$ Joules/gm. mole | K | β Joules/cc | β' Joules/cc |
|---|---|---|---|---|
| 303.15 | -31380 | 324 | 9.78 | 7.64 |
| 273.15 | -31380 | 1272 | 9.90 | 7.54 |
| 243.15 | -31380 | 6998 | 10.12 | 9.87 |
| 213.15 | -31380 | 62195 | 10.52 | 12.41 |

Ethanol + Methylcyclohexane

| T,K | $H^{\circ}$ Joules/gm. mole | K | β Joules/cc | β' Joules/cc |
|---|---|---|---|---|
| 303.15 | -31380 | 324 | 9.70 | 6.43 |
| 273.15 | -31380 | 1272 | 9.70 | 6.52 |
| 243.15 | -31380 | 6998 | 9.82 | 9.31 |
| 213.15 | -31380 | 62195 | 10.24 | 12.41 |

correlation of $G^E$ (sum of squares, $\Sigma^2$, 13 per cent decrease; $\beta$, 2 per cent increase) and a significantly worse correlation of the $H^E$ ($\Sigma^2$, 154 per cent increase; $\beta'$, 35 per cent increase). The variation (K at 50°C from 150 to 75) resulted in a much better correlation of $G^E$ ($\Sigma^2$, 65 per cent decrease; $\beta$, 17 per cent increase) but no correlation at all for $H^E$ ($\Sigma^2$, 2000 per cent increase, $\beta' = 0$). The third variation (A from -20 to 100 Joules/mole-K) was only investigated for the more sensitive $H^E$ data. At 50 Joules/mole-K the best correlation of $H^E$ was obtained with $\Sigma^2$ decreasing by 5 per cent and $\beta'$ increasing by 7 per cent. Therefore the correlation is improved slightly if $H^o$ is allowed to be temperature dependent. It is felt, however, that the slight improvement does not warrant the addition a new adjustable parameter.

The parameters in Table 39 were used to calculated the excess Gibbs free energy and excess enthalpy. The results of the calculations of the chemical and physical contributions to the respective excess property are compared to the derived excess property in Tables 40 and 41.

## Mole Fraction Model

The parameters $K_2$, $K_3$, $H_2$, and $H_3$ had to be determined. If $H_2$ and $H_3$ have the following temperature dependence

$$H_i(T) = H_i(T_o) + A_i(T - T_o) \qquad (75)$$

then the van't Hoff relation can be integrated to give

Table 40. Comparison of $G^E$ From the Volume Fraction Associated Theory of Solutions with $G^E$ Derived From $C_p^E$.*

Ethanol + n-Heptane

| | T = 303.15 K | | | | T = 273.15 K | | | |
|---|---|---|---|---|---|---|---|---|
| $x_a$ | $G_c^E$ | $G_p^E$ | $G_{calc.}^E$ | $G_{der}^E$ | $G_c^E$ | $G_p^E$ | $G_{calc.}^E$ | $G_{der}^E$ |
| 0.1023 | 659 | 56 | 716 | 669 | 625 | 55 | 680 | 639 |
| 0.2805 | 1143 | 140 | 1282 | 1259 | 1069 | 137 | 1206 | 1184 |
| 0.4388 | 1257 | 193 | 1450 | 1448 | 1170 | 189 | 1359 | 1355 |
| 0.6140 | 1133 | 217 | 1350 | 1353 | 1051 | 212 | 1263 | 1266 |
| 0.8107 | 709 | 173 | 882 | 915 | 655 | 169 | 824 | 858 |

| | T = 243.15 K | | | | T = 213.15 K | | | |
|---|---|---|---|---|---|---|---|---|
| $x_a$ | $G_c^E$ | $G_p^E$ | $G_{calc.}^E$ | $G_{der}^E$ | $G_c^E$ | $G_p^E$ | $G_{calc.}^E$ | $G_{der}^E$ |
| 0.1023 | 573 | 55 | 628 | 589 | 510 | 55 | 565 | 530 |
| 0.2805 | 972 | 136 | 1108 | 1086 | 861 | 137 | 998 | 978 |
| 0.4388 | 1061 | 187 | 1248 | 1243 | 939 | 189 | 1127 | 1121 |
| 0.6140 | 950 | 210 | 1160 | 1164 | 840 | 212 | 1052 | 1055 |
| 0.8107 | 591 | 167 | 758 | 794 | 522 | 168 | 690 | 728 |

* Units of $G^E$ are Joules/mole.

2-Propanol + n-Heptane

| | T = 303.15 K | | | | T = 273.15 K | | | |
|---|---|---|---|---|---|---|---|---|
| $x_a$ | $G_c^E$ | $G_p^E$ | $G_{calc.}^E$ | $G_{der}^E$ | $G_c^E$ | $G_p^E$ | $G_{calc.}^E$ | $G_{der}^E$ |
| 0.0809 | 510 | 38 | 548 | 511 | 499 | 38 | 537 | 500 |
| 0.2492 | 986 | 103 | 1089 | 1044 | 942 | 104 | 1047 | 1004 |
| 0.4219 | 1124 | 148 | 1272 | 1251 | 1064 | 150 | 1214 | 1195 |
| 0.5993 | 1016 | 164 | 1180 | 1201 | 957 | 165 | 1122 | 1143 |
| 0.7984 | 641 | 127 | 768 | 812 | 601 | 128 | 729 | 770 |

(Continued)

Table 40. Comparison of $G^E$ From the Volume Fraction Associated Theory of Solutions with $G^E$ Derived From $C_p^E$. (Continued)

| | T = 243.15 K | | | | T = 213.15 K | | | |
|---|---|---|---|---|---|---|---|---|
| $x_a$ | $G_c^E$ | $G_p^E$ | $G_{calc.}^E$ | $G_{der}^E$ | $G_c^E$ | $G_p^E$ | $G_{calc.}^E$ | $G_{der}^E$ |
| 0.0809 | 466 | 38 | 504 | 467 | 419 | 39 | 457 | 423 |
| 0.2492 | 868 | 104 | 972 | 936 | 773 | 106 | 879 | 850 |
| 0.4219 | 974 | 150 | 1124 | 1107 | 865 | 152 | 1017 | 1000 |
| 0.5993 | 873 | 165 | 1038 | 1056 | 774 | 167 | 941 | 956 |
| 0.7984 | 547 | 127 | 674 | 711 | 484 | 129 | 612 | 646 |

| | T = 183.15 K | | | |
|---|---|---|---|---|
| $x_a$ | $G_c^E$ | $G_p^E$ | $G_{calc.}^E$ | $G_{der}^E$ |
| 0.0809 | 362 | 41 | 403 | 373 |
| 0.2492 | 665 | 113 | 778 | 756 |
| 0.4219 | 742 | 162 | 904 | 885 |
| 0.5993 | 662 | 177 | 840 | 853 |
| 0.7984 | 413 | 136 | 549 | 582 |

(Continued)

Table 40. Comparison of $G^E$ From the Volume Fraction Associated Theory of Solutions with $G^E$ Derived From $C_p^E$. (Continued)

Ethanol + Methylcyclohexane

| | T = 303.15 K | | | | T = 273.15 K | | | |
|---|---|---|---|---|---|---|---|---|
| $x_a$ | $G_c^E$ | $G_p^E$ | $G_{calc.}^E$ | $G_{der}^E$ | $G_c^E$ | $G_p^E$ | $G_{calc.}^E$ | $G_{der}^E$ |
| 0.0742 | 521 | 41 | 562 | 542 | 496 | 40 | 535 | 516 |
| 0.1979 | 955 | 102 | 1056 | 1029 | 896 | 99 | 995 | 969 |
| 0.3456 | 1182 | 159 | 1341 | 1325 | 1102 | 154 | 1256 | 1238 |
| 0.5324 | 1173 | 200 | 1374 | 1374 | 1089 | 194 | 1283 | 1284 |
| 0.8004 | 698 | 162 | 859 | 897 | 645 | 156 | 801 | 839 |

| | T = 243.15 K | | | | T = 213.15 K | | | |
|---|---|---|---|---|---|---|---|---|
| $x_a$ | $G_c^E$ | $G_p^E$ | $G_{calc.}^E$ | $G_{der}^E$ | $G_c^E$ | $G_p^E$ | $G_{calc.}^E$ | $G_{der}^E$ |
| 0.0742 | 456 | 39 | 495 | 474 | 406 | 39 | 445 | 423 |
| 0.1979 | 817 | 97 | 914 | 887 | 725 | 98 | 823 | 798 |
| 0.3456 | 1001 | 151 | 1152 | 1133 | 886 | 153 | 1039 | 1019 |
| 0.5324 | 986 | 190 | 1177 | 1178 | 872 | 192 | 1065 | 1066 |
| 0.8004 | 582 | 153 | 736 | 774 | 515 | 155 | 670 | 708 |

Table 41. Comparison of $H^E$ Calculated From the Volume Associated Theory of Solutions with $H^E$ Derived From $C_p^E$.*

Ethanol + n-Heptane

| | T = 303.15 K | | | | T = 273.15 K | | | |
|---|---|---|---|---|---|---|---|---|
| $x_a$ | $H_c^E$ | $H_p^E$ | $H_{calc}^E$ | $H_{der.}^E$ | $H_c^E$ | $H_p^E$ | $H_{calc}^E$ | $H_{der.}^E$ |
| 0.1023 | 431 | 44 | 475 | 507 | 228 | 42 | 270 | 256 |
| 0.2805 | 557 | 109 | 666 | 664 | 289 | 105 | 393 | 374 |
| 0.4388 | 536 | 151 | 687 | 670 | 277 | 144 | 421 | 399 |
| 0.6140 | 435 | 169 | 605 | 593 | 224 | 162 | 385 | 387 |
| 0.8107 | 248 | 135 | 383 | 408 | 127 | 129 | 256 | 298 |

| | T = 243.15 K | | | | T = 213.15 K | | | |
|---|---|---|---|---|---|---|---|---|
| $x_a$ | $H_c^E$ | $H_p^E$ | $H_{calc}^E$ | $H_{der.}^E$ | $H_c^E$ | $H_p^E$ | $H_{calc}^E$ | $H_{der.}^E$ |
| 0.1023 | 100 | 54 | 153 | 136 | 34 | 65 | 99 | 91.6 |
| 0.2805 | 125 | 133 | 258 | 242 | 42 | 162 | 204 | 194 |
| 0.4388 | 119 | 182 | 302 | 280 | 40 | 222 | 263 | 239 |
| 0.6140 | 96 | 205 | 301 | 302 | 32 | 250 | 282 | 278 |
| 0.8107 | 54 | 163 | 218 | 260 | 18 | 198 | 217 | 259 |

* Unites of $H^E$ are Joules/gm. mole

(Continued)

Table 41. Comparison of $H^E$ Calculated From the Volume Associated Theory of Solutions with $H^E$ Derived From $C_p^E$. (Continued)

2-Propanol + n-Heptane

| | T = 303.15 K | | | | T = 273.15 K | | | |
|---|---|---|---|---|---|---|---|---|
| $x_a$ | $H_c^E$ | $H_p^E$ | $H_{calc}^E$ | $H_{der.}^E$ | $H_c^E$ | $H_p^E$ | $H_{calc}^E$ | $H_{der.}^E$ |
| 0.0809 | 536 | 45 | 581 | 558 | 295 | 33 | 328 | 283 |
| 0.2492 | 750 | 124 | 875 | 844 | 400 | 90 | 490 | 490 |
| 0.4219 | 732 | 179 | 911 | 910 | 386 | 130 | 515 | 515 |
| 0.5993 | 595 | 197 | 792 | 809 | 311 | 143 | 454 | 460 |
| 0.7984 | 342 | 153 | 494 | 506 | 178 | 110 | 288 | 294 |

| | T = 243.15 K | | | | T = 213.15 K | | | |
|---|---|---|---|---|---|---|---|---|
| $x_a$ | $H_c^E$ | $H_p^E$ | $H_{calc}^E$ | $H_{der.}^E$ | $H_c^E$ | $H_p^E$ | $H_{calc}^E$ | $H_{der.}^E$ |
| 0.0809 | 132 | 35 | 167 | 140 | 45 | 42 | 88 | 81.3 |
| 0.2492 | 175 | 96 | 271 | 296 | 60 | 115 | 175 | 204 |
| 0.4219 | 168 | 138 | 306 | 296 | 57 | 166 | 223 | 201 |
| 0.5993 | 135 | 152 | 287 | 283 | 46 | 182 | 228 | 222 |
| 0.7984 | 77 | 117 | 194 | 199 | 26 | 140 | 166 | 178 |

| | T = 183.15 K | | | |
|---|---|---|---|---|
| $x_a$ | $H_c^E$ | $H_p^E$ | $H_{calc}^E$ | $H_{der.}^E$ |
| 0.0809 | 11 | 52 | 63 | 59.1 |
| 0.2492 | 14 | 142 | 156 | 174 |
| 0.4219 | 13 | 204 | 217 | 187 |
| 0.5993 | 11 | 223 | 234 | 232 |
| 0.7984 | 6 | 171 | 177 | 202 |

(Continued)

Table 41. Comparison of $H^E$ Calculated From the Volume Associated Theory of Solutions with $H^E$ Derived From $C_p^E$. (Continued)

Ethanol + Methylcyclohexane

| | T = 303.15 K | | | | T = 273.15 K | | | |
|---|---|---|---|---|---|---|---|---|
| $x_a$ | $H_c^E$ | $H_p^E$ | $H_{calc}^E$ | $H_{der.}^E$ | $H_c^E$ | $H_p^E$ | $H_{calc}^E$ | $H_{der.}^E$ |
| 0.0742 | 364 | 27 | 391 | 403 | 194 | 27 | 221 | 190 |
| 0.1979 | 500 | 67 | 568 | 563 | 262 | 66 | 328 | 303 |
| 0.3456 | 525 | 106 | 631 | 607 | 273 | 104 | 376 | 346 |
| 0.5324 | 457 | 133 | 590 | 587 | 236 | 130 | 367 | 373 |
| 0.8004 | 238 | 107 | 345 | 373 | 122 | 105 | 227 | 273 |

| | T = 243.15 K | | | | T = 213.15 K | | | |
|---|---|---|---|---|---|---|---|---|
| $x_a$ | $H_c^E$ | $H_p^E$ | $H_{calc}^E$ | $H_{der.}^E$ | $H_c^E$ | $H_p^E$ | $H_{calc}^E$ | $H_{der.}^E$ |
| 0.0742 | 85 | 37 | 122 | 89 | 29 | 48 | 77 | 54 |
| 0.1979 | 114 | 92 | 206 | 187 | 39 | 119 | 157 | 149 |
| 0.3456 | 118 | 144 | 262 | 232 | 40 | 185 | 225 | 197 |
| 0.5324 | 102 | 181 | 282 | 288 | 34 | 233 | 268 | 268 |
| 0.8004 | 53 | 145 | 198 | 241 | 18 | 188 | 206 | 244 |

$$\text{Ln}\,\frac{K(T)}{K(T_o)} = \frac{(-H_i(T_o) + A_i T_o)}{R}\,\frac{T_o - T}{T\,T_o} + \frac{A_i}{R}\,\text{Ln}\,\frac{T}{T_o} \qquad (76)$$

where i = 2 or 3.

This reduced to the problem of determining $A_2$, $A_3$, and $K_2$, $K_3$, $H_2$, $H_3$ at $T_o$. Haskell et al.[18] give the parameters at 288.15 K for ethanol + n-heptane as $A_2$ = 7.50 cal./deg., $A_3$ = -3.83 cal./deg., $K_2$ = 53.88, $K_3$ = 76.80, $H_2$ = -8850 cal., and $H_3$ = -5500 cal.

The parameters $K_2$, $K_3$, $H_2$, and $H_3$ at other temperatures were

calculated using Equations (75) and (76). The parameters for ethanol + n-heptane used in this work are given in Table 42 at 303.15, 273.15, 243.15, and 213.15 K.

Table 42. Parameters of the Mole Fraction Associated Theory Model.

| T,K | $K_2$ | $H_2$, Joules | $K_3$ | $H_3$, Joules |
|---|---|---|---|---|
| 303.15 | 25.20 | -36558 | 47.63 | -23252 |
| 273.15 | 126.60 | -37499 | 129.78 | -22772 |
| 243.15 | 997.04 | -38440 | 441.17 | -22291 |
| 213.15 | 14991 | -39382 | 2046 | -21810 |

To calculate the excess Gibbs free energy or excess enthalpy, the final monomer mole fraction had to be determined. This involved the solution of a cubic equation. From the overall mass balance

$$\sum_i x_i + x_h^f = 1 \tag{77}$$

and the mass balance of R-OH molecules

$$\sum_i i\, x_i^f = (x_a/x_h)x_h^f \tag{78}$$

the variable $x_h^f$ was eliminated. As shown in Chapter V the following cubic equation was derived

$$a \cdot y^3 + b \cdot y^2 + c \cdot y + d = 0 \tag{79}$$

where

$$a = K_3(K_3 - K_2)$$

$$b = -((K_3^2 + K_2)\cdot x_a + 2\cdot(K_3 - K_2))$$

$$c = 1 + 2\cdot K_3 \cdot x_a$$

$$d = -x_a$$

$$y = x_1^f \quad .$$

As an example case for the ethanol + n-heptane system at 303.15 K, the equilibrium constants were a $K_2$ of 25.20 and a $K_3$ of 47.63. For a mole fraction of ethanol of 0.1023 the roots of the cubic equation were

$$(x_1^f) = 0.01513475$$

$$(x_1^f)' = 0.02910252$$

$$(x_1^f)'' = 0.21740041 \quad .$$

The third root was eliminated since $x_1^f$ must be less than or equal to $x_a$; the second root was eliminated since either Equation (77) or (78) predicts $x_h^f$ is less than $1 - x_a$; and the first root, which satisfied all criteria, was the only physically significant root.

An alternate method of determining the final monomer mole fraction involved solving Equations (77) and (78) by trial and error to determine the roots $x_1^f$ and $x_h^f$ simultaneously. This is illustrated graphically in Figure 11 where the physically significant root is shown. As illustrated in the Figure, Equation (78) is more sensitive

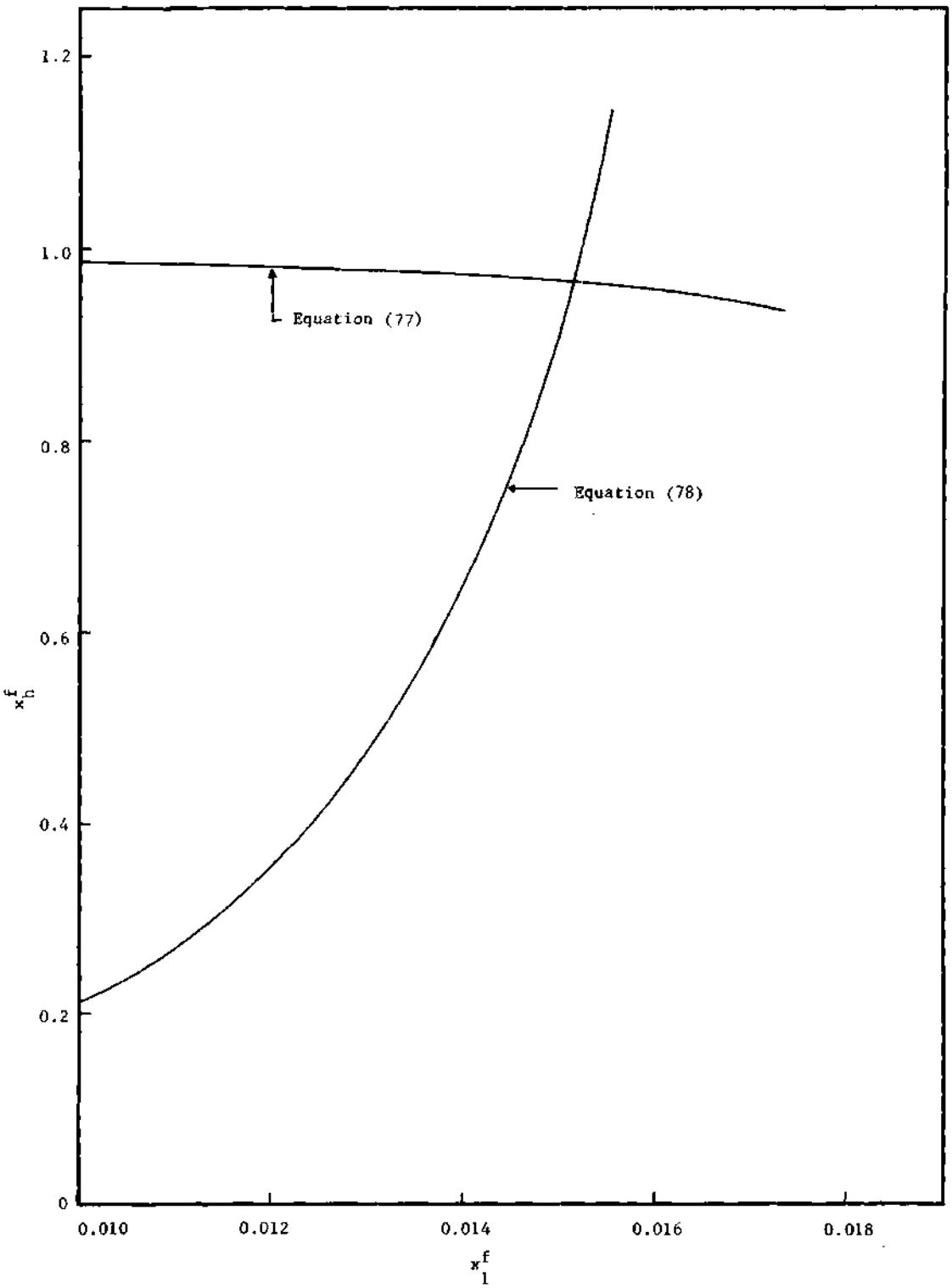


Figure 11. Determination of $x_1^f$ and $x_h^f$ for Ethanol + n-Heptane.

to the choice of $x_1^f$ than is Equation (77). In fact Equation (78) is also more sensitive to the equilibrium constants.

The excess Gibbs free energy and excess enthalpy calculated from Equations (41) and (49) in Chapter V are compared to the derived property in Tables 43 and 44. The derived property is from Appendix C.

Table 43. Comparison of $G^E$ Calculated From the Mole Fraction Associated Theory of Solutions with $G^E$ Derived From $C_p^E$.*

Ethanol + n-Heptane

| T = | 303.15 K | | 273.15 K | | 243.15 K | | 213.15 K | |
|---|---|---|---|---|---|---|---|---|
| $x_a$ | $G^E_{calc}$ | $G^E_{der}$ | $G^E_{calc}$ | $G^E_{der}$ | $G^E_{calc}$ | $G^E_{der}$ | $G^E_{calc}$ | $G^E_{der.}$ |
| 0.1023 | 668 | 669 | 638 | 639 | 589 | 589 | 528 | 530 |
| 0.2805 | 1255 | 1259 | 1179 | 1184 | 1079 | 1086 | 963 | 978 |
| 0.4388 | 1465 | 1448 | 1370 | 1355 | 1251 | 1243 | 1116 | 1121 |
| 0.6140 | 1426 | 1353 | 1331 | 1266 | 1215 | 1164 | 1084 | 1055 |
| 0.8107 | 1024 | 915 | 955 | 858 | 874 | 794 | 781 | 728 |

* Units of $G^E$ are Joules/gm. mole

Table 44. Comparison of $H^E$ Calculated From the Mole Fraction Associated Theory of Solutions with $H^E$ Derived From $C_p^E$.*

Ethanol + n-Heptane

| T = | 303.15 K | | 273.15 K | | 243.15 K | | 213.15 K | |
|---|---|---|---|---|---|---|---|---|
| $x_a$ | $G^E_{calc}$ | $G^E_{der}$ | $G^E_{calc}$ | $G^E_{der}$ | $G^E_{calc}$ | $G^E_{der}$ | $G^E_{calc}$ | $G^E_{der.}$ |
| 0.1023 | 507 | 507 | 264 | 256 | 133 | 136 | 67 | 91.6 |
| 0.2805 | 653 | 664 | 358 | 374 | 195 | 242 | 103 | 194 |
| 0.4388 | 665 | 670 | 377 | 399 | 212 | 280 | 116 | 239 |
| 0.6140 | 603 | 593 | 354 | 387 | 205 | 302 | 114 | 278 |
| 0.8107 | 438 | 408 | 233 | 298 | 160 | 260 | 91 | 259 |

* Units of $H^E$ are Joules/gm. mole

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# VITA

George Nelson Brown, Jr. was born June 30, 1944 at Fort Moultrie, South Carolina. Since his father was in the U.S. Army, he lived in many places both in the United States and abroad during his childhood. A few of the places include Aberdeen, Maryland; Saluda, South Carolina; San Antonio, Texas; Regensburg, and Augsburg, Germany; and Tokyo, and Zama, Japan. He graduated from A. C. Flora High School in Columbia, South Carolina in 1962. From 1962 to 1966 he attended the University of South Carolina where he received a Bachelor of Science degree in Chemical Engineering. His undergraduate thesis, entitled Purification of Industrial Wastes by Ion Exchange was done under the supervision of Dr. M. W. Davis.

He enrolled in the Graduate Division of the Georgia Institute of Technology in 1966 and was awarded an N.D.E.A. fellowship for three years. He received the degree of Master of Science in Chemical Engineering in September, 1967. From 1969 to 1970 he was employed as a graduate teaching assistant in the School of Chemical Engineering.

He was married in September, 1965 to the former Barbara Woodward Barnwell. In May, 1969 they were blessed with a baby girl, Catherine Guerry.